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SAMPLE ANALYSIS FOR K-AR STUDIES OF PALO DURO BASIN BEDDED SALTS

Technical Report

October 1987

J. M. Wampler and Charles E. Weaver

of

Georgia Institute of Technology

Prepared for

UNC Geotech

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ABSTRACT

Clay samples from the San Andres formation contain potassium in at least three minerals, mostly in illite. The sharpness of the x-ray reflections suggests that the illite is detrital. Potassium-argon ages for <2-μm clay samples are nearly all intermediate between the age of the formation (about 255 Ma) and the apparent ages of coarser, detrital material in the rock (about 345 Ma), evidence that diagenetic change has been minimal. A generally good correlation of $^{40}Ar/^{36}Ar$ with $^{40}K/^{36}Ar$ is evident in material released by stepwise dissolution of specimens of recrystallized bedded salt. If data for certain steps are combined, because some potassium was probably carried over from one step to the next whenever a millimeter-sized fluid inclusion opened, the correlation becomes good for four of the five specimens analysed. For three specimens, the lines that best fit the data may be interpreted as internal isochrons for rock that formed in the Permian Period. The two other specimens show evidence of slight disturbance. The potassium-argon ages and the amounts and isotopic composition of argon present initially, suggest that the halite crystals and the millimeter-sized fluid inclusions formed during low-temperature diagenesis soon after deposition of the rock.

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1 INTRODUCTION

Mineralogical and isotopic analyses of salt core samples from the Palo Duro Basin, Texas, were undertaken to aid in the characterization of Permian, San Andres Formation salt rock horizons that may be suitable for the long-term storage of high-level nuclear waste. Samples were provided by the Texas Bureau of Economic Geology, Well Sample and Core Library. Samples studied are from the Grabbe #1 well in Swisher County and the J. Friemel #1 well in Deaf Smith County.

The investigation was divided into two parts. One part was to determine the significance of potassium-argon apparent ages obtained from the illitic clay minerals. The second part was to evaluate the feasibility of obtaining meaningful potassium-argon data from the water-soluble salt and from fluid inclusions. The questions to be addressed were as follows:

(1) Do potassium and ^{40}Ar exhibit correlated release behavior in their siting within the salt, fluid inclusions in salt, and clay?

(2) Have metamorphic and/or water-rock interactions led to the redistribution of potassium and ^{40}Ar?

(3) Do isochrons exist for the samples ($^{40}Ar/^{36}Ar$ versus $^{40}K/^{36}Ar$) and, if so, how well can they be determined?

(4) What are the geochronological implications of the analytical results? Is there evidence for dissolution and recrystallization of the salt? If so, when did it occur?

A new procedure in which potassium and argon are released by stepwise dissolution of rock salt specimens was used to examine the potassium-argon relations in the salt and in fluid inclusions within the salt. By dissolving specimens in a stepwise manner, the potassium and argon from the larger fluid inclusions can be partially separated for analysis from the potassium and argon within the solid salt. Stepwise dissolution also allows a determination of whether the argon isotopes and potassium are distributed within a specimen in a way that defines an isochron. An important aspect of the procedure is that each specimen remains in vacuum between the several steps of dissolution, so there is no opportunity for the specimen to be contaminated with atmospheric argon between steps. Although the argon released from the dissolving salt may be measured at the end of each step, the potassium is in a brine formed by the dissolved salt and cannot be removed right away. But by isolating the

brine formed in each step from that formed in the other steps, the potassium content of each portion of the dissolved salt can be determined later.

Some salt specimens were crushed in vacuum, in a preliminary search for fluid inclusions having argon enriched in ^{40}Ar relative to atmospheric argon. By identifying salt intervals having such inclusions in advance, it was possible to focus the more time-consuming stepwise dissolution work on specimens that were likely to show useful potassium-argon relations.

2 MINERALOGICAL AND POTASSIUM-ARGON ANALYSES OF CLAY MINERALS

2.1 PROCEDURES

For samples from the Grabbe #1 well, composed primarily of anhydrite or dolomite, it was necessary to dissolve the sulfates and carbonates in order to identify and describe the less abundant silicates. It was not necessary to remove anhydrite or dolomite from the mud-rich samples of the J. Friemel #1 well. A method of sulfate and carbonate removal by refluxing in a 0.2 M EDTA solution, which is non-destructive to clays, was used in this study. The method used is that described by Bodine and Fernalld (1973) and modified by Mullin (1982). The EDTA-insoluble residue was dispersed in distilled water using an ultrasonic system and then centrifuged to obtain the <2-μm and >2-μm fractions. The sediment was recycled several times to fully separate the two fractions.

Water-soluble minerals were removed from the predominantly halite samples before EDTA treatment. Whole specimens of chaotic mudstone salt and massive salt were immersed in beakers of distilled water. After the salt dissolved, any anhydrite bands were left intact with the remaining water-insoluble residue. The dissolved material was decanted and the remaining residue was collected, dried, weighed, finely ground, and treated with EDTA. For some specimens, the anhydrite band in the salt was accessible and sampled directly, so there was no need to dissolve salt from around the band.

Portions of the <2-μm fractions used for x-ray analysis were set aside for subsequent potassium-argon analyses. Thin slabs for preparation of thin sections and specimens for scanning electron microscopy were cut from sections adjacent to the locations of the x-ray samples.

The x-ray diffraction analyses were done with Cu K_α radiation in a Philips-Norelco diffractometer. Oriented samples of the <2-μm and >2-μm fractions were scanned from 2° to 40° (2θ). Bulk samples were scanned from 2° to 50° (2θ). The x-ray patterns indicate that the EDTA treatment did not remove a detectable amount of potassium from the illite, so it is unlikely that the ratio of radiogenic argon to potassium was affected by the treatment.

For all of the clay samples finer than 2 μm, potassium-argon analyses were done by the microanalytical method presented by Wampler et al. (1985) and described step by step in the Quality Assurance Specification that is part of

the contract under which this work was done. Briefly, the procedure involves loading one to ten milligrams of clay in a fused-quartz capsule that will retain all of the potassium while argon is released from the clay by heating. The released argon is mixed with a known amount of an isotopic reference material (virtually pure ^{38}Ar), purified, and isotopically analysed by procedures that are described in more detail in a following section of this report (Section 3.2.2). After the isotopic analysis of argon has been completed, the capsule and its contents are dissolved for potassium analysis by atomic absorption spectrophotometry.

Three samples of material coarser than 2 μm were analysed by the conventional potassium-argon method using procedures slightly modified from those described by Dooley and Wampler (1983). In this work, argon is released by fusion of a sample in a resistance-heated furnace, then purified and measured in the usual way. Potassium is measured in a solution prepared by dissolving a separate sample of the material.

2.2 RESULTS AND DISCUSSION

Samples from eight different horizons in each of the two wells were analysed. The mineralogical data are summarized in Table 2-1 and the potassium-argon data in Table 2-2. Samples from the Grabbe #1 well represent a variety of lithologies: chaotic mudstone-salt, anhydrite, muddy anhydrite, and anhydritic dolomite. All of the J. Friemel #1 samples are "muddy" anhydrite bands, which occur within massive salt and chaotic mudstone-salt.

Illite and quartz are present in all samples. The remaining clays are primarily chloritic material present in varying proportions: discrete chlorite (Ch), swelling chlorite (SCh), chlorite/vermiculite (Ch/V), and chlorite/smectite (Ch/S). The clay suites from the Grabbe samples are more variable than those from the Friemel samples, indicating the chloritic clays have responded to the depositional environments. The abundance of Ch/S in the muddy anhydrite bands in both the Friemel and Grabbe wells suggests chloritization is less advanced in these clay-rich samples. Some kaolinite may be present in the Friemel samples. Minor K-feldspar is present in half of the samples. Its abundance is usually less than five percent.

Table 2-1. Mineralogical Data for Clay Samples From the Palo Duro Basin

Well Cycle	Depth (m)	Size (μm)	Clay Suite	K-spar	"Illite" (%)	C.I.	Lithology
Grabbe #1							
Cycle 5	722.3	<2	SCh,Ch,I	A	37	2.7	Mudstone-salt
	734.9	<2	SCh,Ch,Ch/V,I	P	41	2.0	Anhydrite band
	750.4	<2	SCh,Ch,I	P	43	3.8	Mudstone-salt
Cycle 4	792.4	<2	Ch/S,Ch,I	P	31	2.2	Mudstone-salt
	820.5	<2	SCh/Ch,Ch,I	P	23	2.2	Anhydrite band
	821.1	>2	Ch/S,Ch,I	P	35	2.0	Muddy anhydrite
	823.0	<2	S,Ch,I	P	28	---	Muddy anhydrite
	826.0	<2	I,Ch,Ch/V	P	60	2.7	Anhydrite-dolomite
J. Friemel #1							
Cycle 4	787.3	<2	Ch/S,Ch,I	A	26	2.7	Muddy anhydrite
	796.7	<2	Ch/S,Ch,I	A	12	2.8	Muddy anhydrite
	799.0	<2	Ch/S,Ch,I	A	26	2.8	Muddy anhydrite
	799.4	>2	Ch/S,Ch,I	A	24	1.5	Muddy anhydrite
	799.5	<2	Ch/S,Ch,I	A	15	1.8	Muddy anhydrite
	803.6	<1	Ch/S,Ch,I	A	31	2.8	Muddy anhydrite
	803.6	1-2	Ch/S,Ch,I	P	43	1.5	
	803.6	>2	Ch/S,Ch,I	P	23	1.5	
	823.3	<2	Ch/S,Ch,I	A	36	3.3	Muddy anhydrite
	826.0	<2	Ch/S,Ch,I	A	37	3.5	Muddy anhydrite

SCh = swelling chlorite, Ch = chlorite, Ch/V = chlorite/vermiculite, Ch/S = chlorite/smectite, I = illite, K-spar = K-feldspar; A = absent, P = present; C.I. = Crystallinity Index (peak width at half height of 10Å illite peak, in mm); % illite = based on % K, assuming illite has 10% K_2O and no K-feldspar is present.

Table 2-2. Potassium-Argon Data for Clay Samples From the Palo Duro Basin

Well Cycle	Depth (m)	Size (μm)	Potassium (%)	$^{40}Ar^*/^{40}Ar^{(a)}$ (%)	Apparent Age (Ma)
Grabbe #1					
Cycle 5	722.3	<2	3.1	81.2	296
	734.9	<2	3.4	74.3	293
	750.4	<2	3.6	79.9	254
Cycle 4	792.4	<2	2.6	69.7	322
	820.5	<2	1.92	63.3	314
	821.1	<2	1.95	71.4	311
	821.1	>2	2.92	87.2	347
	823.0	<2	2.3	70.8	284
	826.0	<2	5.0	86.3	295
J. Friemel #1					
Cycle 4	787.3	<2	2.2	73.2	312
	796.7	<2	0.99	64.9	294
	799.0	<2	2.2	48.3	300
	799.4	>2	2.03	69.4	341
	803.6	<1	2.6	36.6	280
	803.6	1-2	3.6	76.5	334
	803.6	>2	1.88	63.7	348
	823.3	<2	3.0	31.6	279
	826.0	<2	3.1	67.3	276

(a) $^{40}Ar^*$ denotes radiogenic argon.

The amount of illite present has been estimated by using the potassium values obtained in the potassium-argon analyses (Table 2-2). It has been assumed that the illite contains 10% K_2O. The assumed value may be one or two percent high, but since some of the potassium is in feldspar and a minor amount is in the chloritic material (based on energy-dispersive x-ray analysis during scanning electron microscopy), the estimates of illite content are probably fairly good. Estimated illite contents range from 12% to 60%.

The crystallinity index (C.I.) is a measure, in millimeters, of the 10Å peak-width at half-height. The peak-width is a function of the temperature of formation of the illite (Weaver and Associates, 1984). Values smaller than 3.0 indicate the illite has been exposed to a burial temperature greater than about 270°C. Since all of the C.I. values are less than 4.0, all of these illites have been exposed to temperatures in excess of about 200°C, suggesting that they did not form in the sediments where they now occur. However, little is known about the nature of illite that might form under evaporitic conditions.

The potassium-argon data and apparent ages are shown in Table 2-2. The samples analysed are from the San Andres Formation of Early Guadalupe age. According to the geological time scale of Harland et al. (1982), the age of the Permian System ranges from 286 to 245 million years (Ma). The age of the San Andres Formation should be approximately 255 Ma. The potassium-argon apparent ages range from 254 to 348 Ma. (One analysed sample has been omitted from the table. It was found to contain almost no radiogenic argon, apparently because it had been heat treated before it was used for the potassium-argon analysis.)

In a detrital clay suite, the detrital character of the material is usually most evident in the coarsest illites. The >2-μm fractions of three samples were analysed. These have greater apparent ages, 341 to 348 Ma, than the fine materials and have narrow 10Å peaks, 1.5 to 2.0 mm. These coarse illites are probably mixtures of some older material with illite that either crystallized or, more likely, recrystallized during late Paleozoic metamorphism. This recrystallization may be related to the tectonic activity that occurred in the Ouachita-Marathon orogenic belt in Early Pennsylvanian time.

Aside from the sample from 750.4 m in the Grabbe #1 well, which has an apparent age of 254 Ma, the <2-μm fractions have apparent ages ranging from 276 to 322 Ma (Permian to Mississippian). These ages are greater than the

depositional age of the San Andres sediments (about 255 Ma) indicating the presence of detrital material. However, most of these apparent ages are closer to 255 Ma than to the apparent age of the coarser material (about 345 Ma), suggesting that much of the illite could be authigenic but that older feldspar, K-bearing chlorites, and detrital illite are increasing the apparent ages of the <2-μm fractions. The apparent age of a finer fraction, the <1-μm fraction from 803.6 m in the J. Friemel #1 well, is only 280 Ma, while the 1- to 2-μm fraction from the same depth has an apparent age of 334 Ma, close to the presumed average apparent age of the source material. This shows that detrital material is a significant part of the <2-μm fraction in one case.

It is of interest to note that the potassium-argon apparent age of the <2-μm fraction of most shales is less than the depositional age (Weaver, 1980), yet in the San Andres formation the apparent ages of this size fraction are greater than the age of the rock. Apparent ages less than the depositional age usually indicate that some diagenesis, formation of illite layers, occurred after deposition and during burial. That the apparent ages of the San Andres illites (<2 μm) are slightly greater than the age of the formation may merely reflect the effect of shallow burial on detrital illite, or it may indicate that they are mixtures of authigenic and detrital illite (and other potassium-bearing phases) having average ages less than that of detrital material and greater than that of authigenic material. It should be noted that there is a good linear relation between the apparent ages and the crystallinity index. As the crystallinity increases, the potassium-argon ages increase.

The sample from 750.4 m in the Grabbe #1 well has an apparent age of 254 Ma, which is the approximate age of the San Andres Formation. As a San Andres age was found for only one sample, it cannot be concluded that the illite is authigenic; however, with the present data there is no proof that it is not authigenic. If authigenic illite is present it could be identified by scanning electron microscopy with energy-dispersive x-ray analysis.

3 POTASSIUM-ARGON ANALYSES OF SALT SPECIMENS

3.1 PREPARATION AND DESCRIPTION OF THE SPECIMENS

The salt specimens used in the stepwise dissolution experiments were taken from two different levels of the Grabbe #1 well, selected from core sections that consist of relatively pure halite. The specimens designated as SDS-5, SDS-6, and SDS-7 were taken from the same level, about 8 cm above a band of gray anhydritic siltstone at the 765.2-m level. Thus these specimens are from a depth of 765.1 m. The specimens designated as SDS-8 and SDS-9 were both taken from just above a gray band at a depth of 792.6 m. In all cases care was taken to avoid using strong force in separating these fragments from the core sections. Fragments were removed by gently separating portions of the salt bounded by already existing fractures. In some cases, some of the salt surrounding the intended specimen was carefully dissolved away in order to allow the specimen to be freed from the core section with minimal force.

After each specimen had been removed from the core, it was examined carefully under a binocular microscope. All of the specimens consisted largely of halite, but each contained a variety of mineral inclusions and fluid inclusions. Each specimen was immersed in ethanol (100%), in which halite is only very slightly soluble, in order to remove superficial contamination before it was placed in the apparatus for stepwise dissolution. In fact, the ethanol served as an excellent medium in which to examine the specimens under the binocular microscope. When each specimen was removed from the ethanol it was immediately dried with cellulose tissue. The amount of salt dissolved by the ethanol is negligible in comparison to the masses of the specimens, but was sufficient that fresh cleavage sufaces were slightly dulled by etching.

A description of each specimen, with information about the distribution of inclusions as seen under the binocular microscope, is given in Table 3-1. Some fractures in the crystals could be seen under the binocular microscope, but most of these appeared to be superficial. Only a few fractures extending more than 2 mm into the salt were noted.

The salt specimens used in the experiments in which salt specimens were crushed to release argon were also from the Grabbe #1 well. Because of the preliminary nature of these experiments, the specimens used were not as fully described as those used for the dissolution experiments. Three specimens from

Table 3-1. Descriptive Information About the Salt Specimens Analysed by Stepwise Dissolution

Sample Name	Depth (m)	Mass (g)	Description
SDS-5	765.1	2.76	Cleavage fragment of a single halite crystal having a variety of small fluid and mineral inclusions. Fluid inclusions were mostly rectangular in outline; the largest was about 1-mm long and contained a small gas bubble. Fluid inclusions were not uniformly distributed but occurred in clusters. A group of very small fluid inclusions of irregular form were distributed along a plane parallel to cleavage. A number of small, irregular inclusions of soluble salt were associated with fine red material (presumably iron oxide).
SDS-6	765.1	2.49	Fragments of two halite crystals joined along an irregular surface. One crystal was unusually pure, having only very small fluid inclusions and little of the common red mineral impurity. The other had many inclusions, fluid and red material, concentrated near the interface between the two crystals. The largest fluid inclusion was about 0.7 mm by 0.5 mm by 0.3 mm, had a gas bubble, and was close to the one other fluid inclusion of appreciable size.
SDS-7	765.1	1.38	Fragment of a single crystal of halite containing an irregular fluid inclusion about 1 mm by 1 mm by 3 mm. A gas bubble moved easily within the liquid. A small salt crystal was included near one corner of the larger crystal along with some red material.
SDS-8	792.6	1.61	Comprised three separate halite crystals joined along somewhat irregular interfaces. Fluid inclusions were mostly quite small and were mostly near a portion of the surface where other small impurities were concentrated (many specks of red material and some black materials). One larger fluid inclusion, which had a gas bubble, was in another part of the specimen.
SDS-9	792.6	1.82	Fragment of a single crystal having an unusual concentration of impurities in a more or less cylindrical zone near its center. Much red material, some dark impurities, and possibly a fluid inclusion of moderate size were present in this zone. Small inclusions were present throughout the specimen and an included salt crystal was present near one corner.

the 792.4-m level were the first to be crushed. The first of these had some fluid inclusions up to about 1 mm in size, but the other two had only smaller inclusions. Three other specimens, all from the 764.9-m level, were crushed. The first of these contained an inclusion with a moveable gas bubble. The two other specimens from 764.9 m contained fluid inclusions of moderate size and some small mineral inclusions.

3.2 ANALYTICAL PROCEDURES

3.2.1 Stepwise Dissolution of Salt

The stepwise dissolution experiments were done in a borosilicate-glass apparatus comprising five vertical cylindrical chambers of 2-cm diameter, called sumps. The sumps are attached to and interconnected by a horizontal cylinder of 3-cm diameter (Figure 3-1). Above each sump is a tube section of 1-cm diameter, which may be opened for removal of liquid from the sump and then resealed. In each sump is a pedestal of borosilicate glass, which is used to hold a salt specimen several centimeters above the bottom of the sump when the sump is in use. Each pedestal has within it a cylindrical piece of iron so that it may be manipulated from outside the apparatus with magnets. Movement of the pedestals in this way is necessary from time to time to stir liquid and to move a specimen from one sump to another.

The apparatus comprising the sumps is connected by a section of capillary tubing to a cold trap and thence to a valve (designated "C1") leading to the vacuum manifold used for purification and isotopic analysis of argon. The capillary tubing serves to prevent excessively rapid flow of gas, and the cold trap keeps water from leaving the apparatus (other than in insignificant amounts) when the valve C1 is open.

The work reported herein is the first in which stepwise dissolution has been used as a means of releasing argon from salt for isotopic analysis. The new procedures used were under development as the work progressed, and so changes in the procedures were introduced as the need for them became evident. Consequently, a detailed description of the procedures used, and a discussion of the phenomena observed during the analyses that led to changes in procedure, are given in an appendix. Following is a brief account of the procedures used.

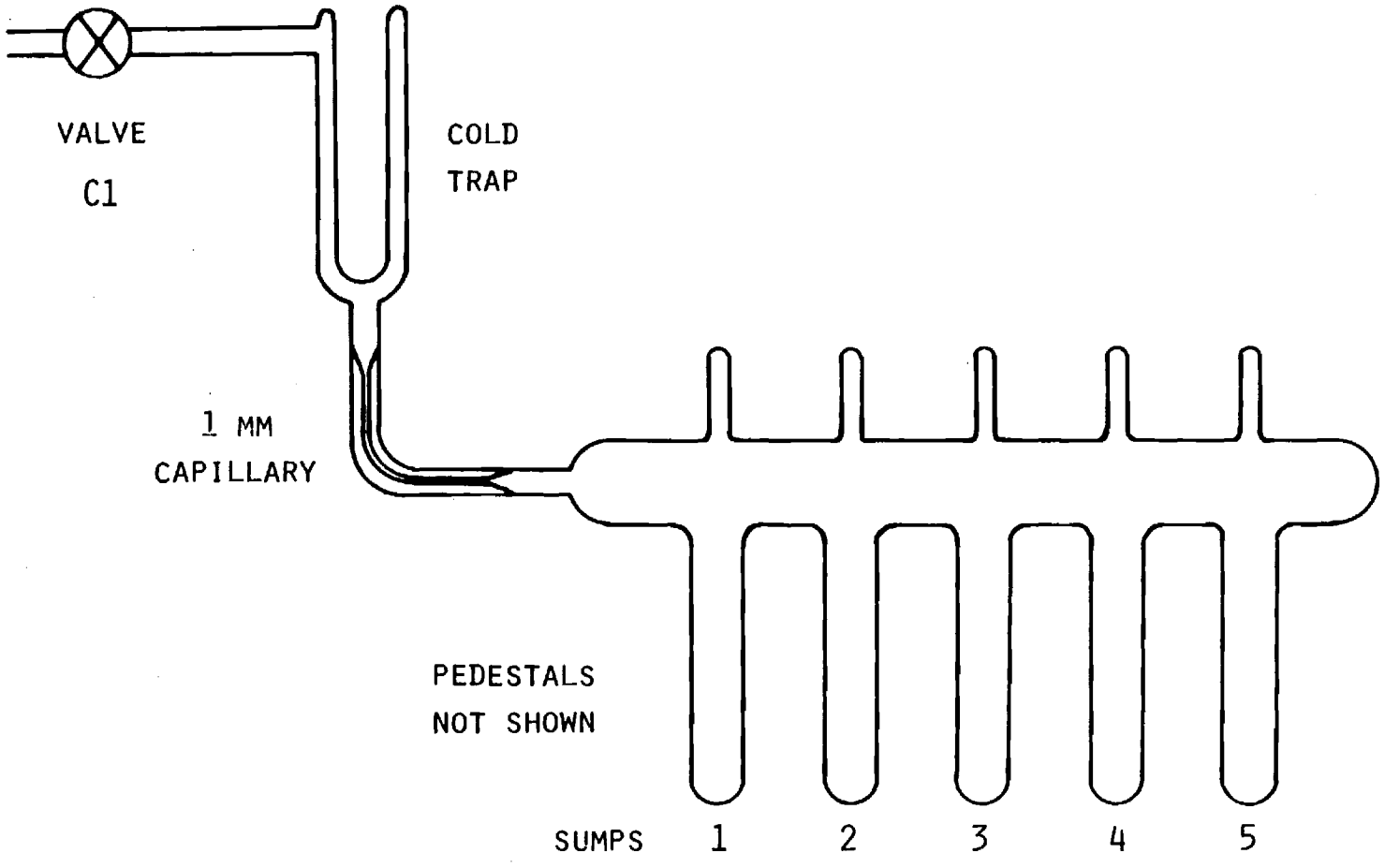

Figure 3-1. Diagram of the Apparatus Used for Stepwise Dissolution of Salt Specimens

To prepare for a stepwise dissolution experiment, several milliliters of distilled water is put in one or more sumps on the left side of the apparatus. A salt specimen is then placed in Sump 5 and the apparatus is sealed. With dry ice in the cold trap, the apparatus is evacuated and the water is degassed by stirring and distillation. (After evacuation has begun and before any dissolution of salt is to begin, some portion of the apparatus is always kept cooler than the salt. This keeps the water-vapor pressure always less than that at which water would condense on the salt.) After the contaminating argon in the apparatus has been reduced to a negligible level, as shown by "blank" analyses, the first step in dissolution of the sample can begin.

Dissolution begins with the salt specimen atop the pedestal in Sump 5. Cooling the glass surrounding the specimen causes water to condense there, flow onto the salt, and then drain into the lower part of the sump. To terminate the dissolution, it is necessary only to stop cooling the glass near the specimen and to cool one of the other sumps (not Sump 4) with ice water. The specimen is then transferred to Sump 4 so that it will be ready for the next dissolution step. After the argon released in the first step has been analysed, and any following blank runs have been completed, the following dissolution steps are carried out similarly, progressing from sump to sump so that the salt dissolved in each step will remain separate from that dissolved in other steps.

It should be noted that the brine cannot drain completely from a specimen as a dissolution step is brought to a close. The film of water that does not drain from the specimen will evaporate, leaving a small amount of once-dissolved salt to be carried over with the specimen to the next sump. Thus, the potassium released in one step is not completely separated from that released in the subsequent step.

Before analysis of the argon, it is necessary to distill the water from the brine that has formed during dissolution in order to get all the argon out of the brine. Even after distillation, a significant fraction of the argon may be dissolved in water rather than in the gas phase. Hence, there can be a carry-over of argon from one step to the next unless care is taken to be sure all the argon is out of the water before the next step is begun. In the work reported herein, "blank" runs were carried out after most of the dissolution steps, so carry-over of argon from one step to the next was not usually important.

3.2.2 Isotopic Analysis of Argon

Immediately before each sample of argon is released from the dissolution apparatus, a valve is closed to isolate the vacuum manifold where the argon is to be mixed with the reference isotope ^{38}Ar and purified prior to the isotopic analysis. Then a known amount of the isotopic reference material is released from a reservoir into the manifold, and the valve C1 is opened so that the gases released during dissolution may flow into the manifold. A cold trap at -112°C collects the small amount of water vapor that the trap within the dissolution apparatus does not hold. A second cold trap at -183°C collects carbon dioxide and any other gases condensible at this temperature, and the remaining non-inert gases are removed by reaction with hot titanium. (Because the amounts of gas released by the salt specimens used in this study were generally quite small, only a minute or two was required for purification.)

The argon mixture is then admitted to the mass spectrometer for isotopic analysis, according to procedures that are standard in this laboratory. These procedures ensure that there is no isotopic fractionation during the transfer, that the amount of argon transferred to the mass spectrometer does not exceed the maximum amount measurable by the instrument, and that the amount of argon can be determined with reasonable accuracy even when the isotopic reference material has not been used (which was the case for all of the blank runs).

The MS-10 mass spectrometer used for the isotopic analysis of argon is well suited for measurement of small amounts of argon in the static mode, because of the virtual absence of a "memory effect" (Farrar et al., 1964). The detection limit for ^{36}Ar is about 0.1 fmol (1 fmol = 10^{-15} mol), which means the detection limit for radiogenic argon is about 30 fmol. Corrections for mass discrimination and for interfering background signals are normally quite small, but errors caused by these phenomena may be larger than normal just before failure of the ion-source filament and for some time after its replacement. Such a failure occurred, unfortunately, during this work. For this reason, and because in some cases the amount of ^{36}Ar was not far above the detection limit, the errors estimated for the argon isotopic analyses in this work are relatively large.

3.2.3 Potassium Analysis

When the stepwise dissolution of a specimen has been completed, the salt accumulated in each sump is removed in aqueous solution, separated from any water-insoluble residue that may be present, and recovered as solid salt by evaporation of the water. After the salt has been weighed, it is dissolved in enough water (containing a small amount, 2.5 mmol/kg, of CsCl) to form a solution having one hundred times the mass of the original salt. The potassium content of each solution is determined by atomic absorption spectrophotometry, by comparison with reference solutions containing NaCl (10 g/kg), CsCl (2.5 mmol/kg), and potassium in amounts ranging up to 2 mg/kg.

Because of the low levels of potassium in the salt samples analysed in this work, the effects of contamination and of instrumental noise on these analyses are relatively large. Hence, the estimated relative errors for these potassium measurements are larger than those normally encountered in potassium-argon work.

3.2.4 Procedure for Crushing Specimens in Vacuum

The apparatus in which specimens were crushed to release argon from fluid inclusions was an all-metal apparatus connected to the same valve (C1, see Figure 3-1) that was later used for the stepwise dissolution experiments. Specimens were crushed by driving a piston (attached to the specimen holder by a flexible metal bellows) down onto the salt with light blows from a hammer.

The crushing experiments were done with the valve C1 open so that the effect of crushing could be monitored by the response of an ionization gauge to the gases released. By thus noting the size of the pulse of gas released upon each hammer blow, some feeling for the amount of force necessary to break open the specimens was developed, even though no provision had been made for actually viewing the specimens within the sealed apparatus.

Argon released in the crushing experiments was isotopically analysed in the manner described above for argon released by stepwise dissolution. Several of the crushed specimens were immersed in absolute ethanol, after they had been removed from the apparatus, in an attempt to extract the potassium that had been present in the fluid inclusions that were opened during the crushing. The ethanol was later evaporated away from the extracted salt, and that salt

(of the order of 100 mg) was redissolved in an aqueous medium for potassium analysis by atomic absorption spectrophotometry.

3.3 RESULTS

3.3.1 Observations Made During Dissolution of the Specimens

The potassium-argon data obtained by stepwise dissolution of the five salt specimens described in Section 3.1 are given in Tables 3-2 through 3-6. In these tables, the first column of analytical data gives the amount of dry salt recovered from the solution produced in each step. For most specimens, the total amount of salt recovered from all the steps agrees well with the original mass of the specimen, given that there is a 0.01-g uncertainty in each weighing. The greatest discrepancy is in the case of specimen SDS-7, for which only 1.30 g of salt was recovered from a 1.38-g specimen. Although this specimen contained a fluid inclusion larger than that in any other specimen, the inclusion was not large enough to account for the 0.08-g difference between the masses of the original specimen and the recovered salt.

Although the first step in dissolution was normally one in which only a small amount of salt was dissolved, this practice was not followed in the case of the first specimen, SDS-5, from which 0.31 g was dissolved in the first step. Comparable amounts were dissolved in the next three steps, leaving a disproportionate amount, 1.45 g, to be dissolved in the final step. The largest fluid inclusion in SDS-5 had originally been near one face, which was the upper surface as the the specimen was oriented in the apparatus. Observation indicated that the inclusion was still unopened at the end of the second step; it probably opened during the third step, in which a deliberate attempt was made to dissolve salt from the upper surface.

SDS-6 was the only specimen for which more than five steps were used in dissolution, which was a consequence of an attempt to control the dissolution in such a way that the argon to be released from the largest fluid inclusion could be well resolved from other argon within the specimen. Since the apparatus has only five sumps, it was necessary to open the apparatus after the fifth step in order to remove the salt that had been dissolved from the specimen in the first five steps. Because of possible contamination of the specimen with atmospheric argon during this process, the amount of salt dissolved

Table 3-2. Potassium-Argon Data From Stepwise Dissolution of SDS-5

Step	Amount Dissolved (g)	Potassium (μg)	Potassium (mg/kg)	$^{40}K/^{36}Ar$ x 10^{-3}	$^{40}Ar/^{36}Ar$	Correlation Factor	$^{40}Ar^*/^{40}Ar$ (%)	$^{40}Ar^*$ (pmol)	Apparent Age (Ma)
1	0.31	27.7 ± 0.6	89	7.95 ± 0.50	339 ± 13	0.39	12.9	0.45 ± 0.13	92 ± 26
Blank 1					331 ± 13		10.8	0.36 ± 0.12	
Blank 2					319 ± 20		7.4	0.04 ± 0.03	
Total				3.75 ± 0.16	334 ± 9	0.40	11.5	0.85 ± 0.18	169 ± 35
2	0.21	13.9 ± 0.4	66	0.31 ± 0.01	303 ± 11	0.80	2.4	0.97 ± 1.42	364 ± 482
Blank					310 ± 16		4.5	0.04 ± 0.04	
Total				0.30 ± 0.01	303 ± 11	0.80	2.5	1.01 ± 1.42	378 ± 478
3[(a)]	0.44	30.2 ± 0.9	69	3.03 ± 0.12	374 ± 14	0.84	20.9	2.33 ± 0.36	397 ± 57
Blank					370 ± 30		20.2	0.08 ± 0.02	
Total				2.93 ± 0.11	374 ± 13	0.84	20.9	2.40 ± 0.36	409 ± 57
4	0.35	21.6 ± 0.7	62	8.18 ± 0.37	410 ± 16	0.78	28.0	0.90 ± 0.11	227 ± 26
5	1.45	87.1 ± 2.9	60	7.08 ± 0.30	416 ± 15	0.72	29.0	4.43 ± 0.48	272 ± 28
Blank					261 ± 27		-13.1	-0.02 ± 0.02	
Total				6.96 ± 0.29	413 ± 15	0.72	28.5	4.41 ± 0.48	270 ± 29
Combined steps:									
1-5	2.76	180.5 ± 3.2	65	2.30 ± 0.06	336 ± 7	0.79	12.2	9.57 ± 1.55	282 ± 43
3,4	0.79	51.8 ± 1.1	66	4.00 ± 0.13	381 ± 11	0.84	22.5	3.31 ± 0.38	335 ± 36

(a) The largest fluid inclusion in the specimen opened during the third step of the dissolution.

Table 3-3. Potassium-Argon Data From Stepwise Dissolution of SDS-6

Step	Amount Dissolved (g)	Potassium (µg)	Potassium (mg/kg)	$^{40}K/^{36}Ar$ x 10^{-3}	$^{40}Ar/^{36}Ar$	Correlation Factor	$^{40}Ar^*/^{40}Ar$ (%)	$^{40}Ar^*$ (pmol)	Apparent Age (Ma)
1	0.06	4.2 ± 0.1	70	1.61 ± 0.06	319 ± 8	0.44	7.4	0.18 ± 0.06	236 ± 71
Blank					291 ± 54		-1.5	0.00 ± 0.04	
Total				1.48 ± 0.06	317 ± 9	0.52	6.7	0.18 ± 0.07	232 ± 84
2	0.16	6.5 ± 0.3	41	4.53 ± 0.27	371 ± 13	0.33	20.3	0.32 ± 0.04	266 ± 36
Blank					315 ± 87		6.2	0.01 ± 0.04	
Total				4.10 ± 0.25	366 ± 15	0.45	19.2	0.33 ± 0.06	272 ± 45
3	0.23	11.0 ± 0.5	48	14.46 ± 1.30	534 ± 42	0.78	44.7	0.54 ± 0.05	264 ± 26
Blank					458 ±150		35.5	0.06 ± 0.04	
Total				12.40 ± 1.12	523 ± 43	0.83	43.5	0.60 ± 0.06	291 ± 31
4	0.38	16.2 ± 0.8	43	4.89 ± 0.25	375 ± 8	0.19	21.1	0.78 ± 0.07	259 ± 23
5[(a)]	0.35	35.1 ± 0.7	100	5.20 ± 0.15	414 ± 9	0.54	28.5	2.38 ± 0.13	354 ± 19
Blank					294 ± 56		-0.4	0.00 ± 0.04	
Total				5.04 ± 0.15	410 ± 9	0.55	27.9	2.37 ± 0.14	353 ± 20
6	0.07	7.8 ± 0.4	112	16.46 ± 1.31	440 ± 27	0.59	32.8	0.20 ± 0.03	145 ± 19
7	0.25	18.2 ± 0.5	73	11.78 ± 0.51	414 ± 14	0.60	28.6	0.54 ± 0.05	165 ± 14
8	0.89	37.8 ± 1.8	43	7.79 ± 0.40	409 ± 8	0.14	27.8	1.65 ± 0.08	235 ± 15
Blank					383 ± 19		22.8	0.15 ± 0.03	
Total				6.97 ± 0.32	407 ± 7	0.15	27.3	1.80 ± 0.09	255 ± 16
Combined steps:									
1-8	2.39	136.8 ± 2.2	57	5.94 ± 0.11	395 ± 4	0.34	25.1	6.82 ± 0.21	267 ± 9
5-7	0.67	61.0 ± 0.9	91	6.80 ± 0.16	412 ± 7	0.56	28.3	3.12 ± 0.14	273 ± 12

(a) The largest fluid inclusion in the specimen opened during the fifth step of the dissolution.

Table 3-4. Potassium-Argon Data From Stepwise Dissolution of SDS-7

Step	Amount Dissolved (g)	Potassium (μg)	Potassium (mg/kg)	$^{40}K/^{36}Ar$ x 10^{-3}	$^{40}Ar/^{36}Ar$	Correlation Factor	$^{40}Ar^*/^{40}Ar$ (%)	$^{40}Ar^*$ (pmol)	Apparent Age (Ma)
1	0.04	6.6 ± 0.4	164	5.27 ± 0.36	361 ± 9	0.12	18.1	0.24 ± 0.03	202 ± 24
2[a]	0.37	103.3 ± 1.3	279	8.36 ± 0.16	419 ± 6	0.55	29.5	4.56 ± 0.16	238 ± 8
Blank					413 ± 9		28.5	0.33 ± 0.03	
Total				7.76 ± 0.14	419 ± 5	0.53	29.4	4.90 ± 0.17	255 ± 9
3	0.25	43.0 ± 0.5	172	3.42 ± 0.06	322 ± 4	0.59	8.2	0.98 ± 0.16	127 ± 20
Blank					330 ± 21		10.4	0.04 ± 0.02	
Total				3.32 ± 0.06	322 ± 4	0.59	8.2	1.02 ± 0.16	132 ± 20
4	0.27	20.5 ± 0.5	76	13.08 ± 0.45	489 ± 11	0.41	39.6	0.90 ± 0.03	238 ± 10
Blank					507 ±203		41.7	0.03 ± 0.02	
Total				12.68 ± 0.45	490 ± 12	0.48	39.7	0.94 ± 0.04	246 ± 11
5	0.37	32.9 ± 0.9	89	43.05 ± 1.74	932 ± 27	0.53	68.3	1.45 ± 0.02	238 ± 7
Blank					1229 ±637		76.0	0.11 ± 0.02	
Total				40.97 ± 1.88	947 ± 35	0.67	68.8	1.56 ± 0.03	255 ± 8
Combined steps:									
1-5	1.30	206.2 ± 1.8	159	6.90 ± 0.08	393 ± 3	0.53	24.7	8.66 ± 0.23	227 ± 6
2,3	0.62	146.2 ± 1.4	236	5.57 ± 0.07	371 ± 4	0.56	20.4	5.92 ± 0.23	219 ± 8

(a) The unusually large fluid inclusion in this specimen opened during the second step.

Table 3-5. Potassium-Argon Data From Stepwise Dissolution of SDS-8

Step	Amount Dissolved (g)	Potassium (μg)	Potassium (mg/kg)	$^{40}K/^{36}Ar$ x 10^{-3}	$^{40}Ar/^{36}Ar$	Correlation Factor	$^{40}Ar^*/^{40}Ar$ (%)	$^{40}Ar^*$ (pmol)	Apparent Age (Ma)
1	0.10	8.6 ± 0.4	86	0.82 ± 0.04	306 ± 4	0.07	3.4	0.32 ± 0.12	206 ± 74
Blank					292 ± 13		-1.2	-0.01 ± 0.02	
Total				0.77 ± 0.04	305 ± 4	0.07	3.1	0.32 ± 0.12	202 ± 75
2	0.37	[31.8][(a)]	[86]	[0.61]	299 ± 4	[0.21]	1.2	0.57 ± 0.55	[100]
Blank					306 ± 7		3.3	0.05 ± 0.03	
Total				[0.59]	299 ± 3	[0.21]	1.3	0.62 ± 0.55	[109]
3	0.32	28.3 ± 0.6	89	0.58 ± 0.01	304 ± 4	0.22	2.7	1.21 ± 0.51	230 ± 92
Blank					306 ± 6		3.5	0.08 ± 0.04	
Total				0.56 ± 0.01	304 ± 3	0.22	2.8	1.29 ± 0.51	245 ± 91
4	0.39	39.6 ± 0.8	102	1.24 ± 0.03	313 ± 4	0.29	5.5	1.63 ± 0.36	222 ± 47
Blank					301 ± 11		1.9	0.01 ± 0.02	
Total				1.21 ± 0.03	312 ± 4	0.29	5.4	1.64 ± 0.36	224 ± 47
5	0.41	30.3 ± 0.8	74	3.88 ± 0.12	355 ± 6	0.29	16.8	1.39 ± 0.12	247 ± 21
Blank					343 ± 13		13.7	0.10 ± 0.02	
Total				3.55 ± 0.11	354 ± 6	0.29	16.5	1.49 ± 0.12	263 ± 21
Combined steps:									
1-5	1.59	[138.7]	[87]	[0.88]	307 ± 2	0.21	3.7	5.35 ± 0.85	[210]
1,3-5	1.22	106.8 ± 1.4	88	1.04 ± 0.02	311 ± 2	0.22	4.9	4.73 ± 0.65	239 ± 31

(a) Numbers shown in brackets are based on an assumed value (86 mg/kg) for the potassium content of the salt dissolved in the second step.

Table 3-6. Potassium-Argon Data From Stepwise Dissolution of SDS-9

Step	Amount Dissolved (g)	Potassium (μg)	Potassium (mg/kg)	$^{40}K/^{36}Ar$ x 10^{-3}	$^{40}Ar/^{36}Ar$	Correlation Factor	$^{40}Ar^*/^{40}Ar$ (%)	$^{40}Ar^*$ (pmol)	Apparent Age (Ma)
1	0.05	7.4 ± 0.4	149	0.466 ± 0.026	300 ± 4	0.05	1.7	0.24 ± 0.18	175 ± 124
Blank					316 ± 13		6.4	0.04 ± 0.02	
Total				0.448 ± 0.024	301 ± 4	0.05	1.9	0.28 ± 0.18	202 ± 124
2	0.43	28.4 ± 0.9	66	1.317 ± 0.043	315 ± 4	0.15	6.1	1.23 ± 0.25	234 ± 45
Blank					294 ± 20		-0.5	0.00 ± 0.02	
Total				1.297 ± 0.042	314 ± 4	0.15	6.0	1.23 ± 0.25	233 ± 45
3	0.41	28.0 ± 0.8	68	0.745 ± 0.024	308 ± 4	0.15	4.1	1.42 ± 0.40	272 ± 72
Blank					305 ± 7		3.2	0.03 ± 0.02	
Total				0.724 ± 0.022	308 ± 4	0.15	4.1	1.46 ± 0.41	277 ± 72
4	0.52	33.3 ± 1.0	64	0.821 ± 0.027	304 ± 4	0.13	2.7	1.00 ± 0.43	166 ± 69
Blank					309 ± 6		4.5	0.09 ± 0.04	
Total				0.781 ± 0.025	304 ± 3	0.13	2.8	1.09 ± 0.43	179 ± 68
5	0.40	24.6 ± 0.8	62	0.046 ± 0.002	295 ± 3	0.11	-0.3	-1.47 ± 5.39	-383 ±1564
Blank					299 ± 4		1.1	0.14 ± 0.14	
Total				0.045 ± 0.002	295 ± 3	0.11	-0.3	-1.34 ± 5.40	-344 ±1531
Combined steps:									
1-5	1.81	121.7 ± 1.8	67	0.183 ± 0.005	297 ± 3	0.11	0.5	2.71 ± 5.44	124 ± 240

in the sixth step, as in the first step, was very small (less than 0.1 g in each case). In each of the other steps except the last one, less than 0.4 g of salt was dissolved. During steps 2, 3, and 4, the condensation of water was controlled so that most of the salt dissolved was from the part of the specimen that had few inclusions. In the fifth step, the condensing water was directed to the other crystal, which resulted in the opening of the largest fluid inclusion. The opening of the inclusion, which had a sizeable gas bubble, was quite evident because of splashing of water as gas expanded. The dissolution was stopped promptly after this event was observed in order to examine the argon that had been released. It could not be determined with certainty whether the other fluid inclusion of appreciable size, nearby, opened during this step or during a subsequent step. The part of the specimen that had contained these inclusions was dissolved away during the seventh step. In the eighth step the remainder of the specimen, an amount disproportionately larger that that dissolved in the earlier steps, was dissolved.

Only a small amount of SDS-7 was dissolved in the first step, but roughly equal amounts were dissolved in the subsequent steps. The large fluid inclusion in this specimen opened during the second step, but the fluid was not observed to splash out in the manner that had been expected. The corner of the specimen having an included salt crystal was gone by the end of the third step.

Only a small fraction of SDS-8 was dissolved in the first step of dissolution, but in the subsequent steps the remainder of the specimen was dissolved in roughly equal increments. The part of the specimen that was relatively rich in impurities was dissolved mostly during the third step. It could not be determined in which step the fluid inclusion with the gas bubble dissolved. (This inclusion was not as large as the largest fluid inclusions in other specimens analysed.) Some splashing of water was noted during the last step (in which the specimen was immersed in water at the bottom of a sump), presumably a consequence of the release of small bubbles of gas, but the amount of argon released during this step was less than in each of the steps 2, 3, and 4.

Except for the first step, in which only a little salt was dissolved, SDS-9 was dissolved in roughly equal increments. If (as there appeared to be) there was a fluid inclusion of moderate size within the cylindrical zone where impurities were concentrated in this specimen, it should have opened during

the second step, but no splashing was noted at the time. This specimen developed an unusually irregular form as it progressively dissolved. During the final step, with the specimen immersed in water, several bubbles were seen to be released and to rise through the water.

3.3.2 Results of the Potassium Measurements

The amount of potassium released in each step is given in micrograms and is also given as a mass fraction expressed as milligrams of potassium per kilogram of dissolved salt (parts per million by weight) in Tables 3-2 through 3-6. The uncertainty indicated for the mass of potassium released in each step is an estimate of error based largely on the concentration of potassium in the solution prepared for atomic absorption spectrophotometry. The corresponding relative errors are in the range 1% to 6%. No attempt has been made to include the effect of carry-over of potassium from one step to the next (described in Section 3.2.1) in these estimates of error.

Because of uncertainty in the mass of the recovered salt, the mass fraction of potassium is quite uncertain in cases where only a small amount of salt was dissolved, but in other cases the relative error in the mass fraction should not be more than five percent. The values obtained range from just over 40 mg/kg for several steps in the dissolution of SDS-6 to 279 mg/kg for the second step in the dissolution of SDS-7. The potassium content is fairly uniform for all of the steps in the cases of SDS-5, SDS-8, and SDS-9, disregarding the first step for SDS-9 in which a very small amount of salt was dissolved. (It was not possible to obtain a potassium measurement for the second step in dissolution of SDS-8, because the tube containing the solution broke during centrifuging. Although the solution was recovered from the metal centrifuge-tube holder, it was found to be anomalously rich in potassium, obviously a consequence of contamination.)

For SDS-6 and SDS-7, the potassium released in a few of the steps is more than twice as great, per unit mass of salt dissolved, than in other steps. In each of these cases, the first step having a distinctly elevated level of potassium is one in which a large fluid inclusion opened. It is notable that the potassium content of SDS-6 appears to be quite uniform for the salt dissolved before the inclusion opened (41-48 mg/kg for steps 2, 3, and 4). The potassium content of the salt recovered from the fifth step, during which the

inclusion opened, is more than twice as great (100 mg/kg), and the two following steps also show elevated potassium contents. The potassium content of the salt dissolved in the final step is 43 mg/kg, essentially the same as in the early steps.

The elevated potassium content of the salt dissolved in the fifth step for SDS-6 may be attributed to the influence of the fluid from the large inclusion. The amount of "extra" potassium in this step is about 20 μg, however, which would correspond to a high concentration of potassium in the fluid if the estimated volume of fluid (about 0.1 mm^3) is correct. (The size of the inclusion may have been underestimated as a result of refraction of light within the specimen, and it is likely that a somewhat smaller fluid inclusion near the largest one also opened during this step, so the amount of "extra" potassium inferred may not be unreasonable.) It seems quite likely that the elevated levels of potassium seen in steps 6 and 7 may be a consequence of carry-over of potassium from the fifth step. Since the fifth step was terminated promptly after the large fluid inclusion opened, it seems probable that a significant amount of potassium from the inclusion may have remained with the specimen to be carried over to step 6. Knauth and Beeunas (1986) have noted evidence that hydrous salts precipitate as water evaporates from fluid inclusions opened in vacuum. Some potassium-bearing salt may have precipitated in this case, because the water-vapor pressure in the apparatus was lowered promptly after this fluid inclusion opened. Since only a small amount of salt was dissolved in step 6, and since the opened inclusion had left a re-entrant cavity in the surface of the specimen, it is reasonable to infer that some "extra" potassium may have been carried over to step 7 as well. (These inferences have been influenced by the potassium-argon ratios observed for this specimen. A further discussion follows below after the argon isotope ratios have been introduced.)

The salt dissolved from SDS-7 had an unusually high potassium content in the second step, during which the very large fluid inclusion in this specimen apparently opened, and also in the following step. The mass fraction of potassium in the salt from the second step is more than three times greater than the average for the last two steps, corresponding to about 70 μg of "extra" potassium. The third step also had an elevated level of potassium, and if the "extra" potassium from this step is included, the total of "extra" potassium is about 90 μg, corresponding to a potassium content in the fluid of

about 30 g/kg (3%) if the "extra" potassium was all in the fluid and if the volume of the fluid was correctly estimated as about 3 mm^3. As in the case of SDS-6, it is reasonable to expect that some of the potassium from the inclusion was carried over into the step following the one during which the inclusion opened.

The first specimen analysed, SDS-5, had several fluid inclusions of significant size, but these were probably somewhat smaller than the largest inclusion in SDS-6. The largest inclusion in SDS-5 appeared to have opened during the third dissolution step, but the potassium content of the salt from this step is not appreciably elevated with respect to the other steps. Nor is there any elevation of potassium content in the second step for SDS-9, in which a fluid inclusion of moderate size is thought to have opened.

3.3.3 Results of the Argon Isotopic Measurements

The data in the last six columns of Tables 3-2 through 3-6 are the data needed to construct potassium-argon isotope correlation diagrams and data pertaining to potassium-argon apparent ages calculated in the conventional way. As noted in Section 3.2.1, a blank argon analysis was done after the original argon analysis for most of the dissolution steps, in order to determine the amount of argon that was in solution, rather than in the gas phase, at the time the argon was transferred for the original analysis. (In five cases no blank run was done; in these cases any argon remaining in solution would have been carried over into the next step.) Because significant amounts of argon were found in most of these blank runs, the data from the blank runs are included in the tables. In one case, the first step for the first specimen analysed, data from a second blank run are included. In a number of other cases a second blank was run, but the amount of argon found in each of these is negligible, and so these second blanks are not included in the tables. For each step where blank-run data are given, there follows a row of data based on the total of the argon measured in the original analysis and in the blank run(s).

In some cases, the amount of argon found in a blank run immediately following the original argon analysis for a dissolution step was so small that there is great uncertainty in the measurement of ^{36}Ar. Data from such blank runs are included in the tables to show the full range of the phenomena that

made the blank runs necessary. (Second-blank runs having such small amounts of argon were not included in the tables.) A consequence of the decision to include these blank runs in the tables is that the amount of radiogenic argon calculated for a few of the blank runs is negative, but in no case is the negative amount greater than the error estimated for the calculated value.

The problem of accuracy in measurement of ^{36}Ar was exacerbated in part of this work by problems associated with a failure of the mass spectrometer's filament, including a persistent background spectrum due to organic material in the mass spectrometer after a new filament was installed. The first specimen, SDS-5, was analysed just before the filament failed. A rapid change in ion-source characteristics during the period when this specimen was being analysed has required that unusually large errors be assigned for the $^{40}Ar/^{36}Ar$ ratios for this specimen. The next specimen, SDS-6, was analysed when the problem with the organic backgound spectrum was greatest. In a few of the dissolution steps for this specimen, the amount of ^{36}Ar released was very small, so the estimated error in the $^{40}Ar/^{36}Ar$ ratio is large, as much as 8% in one case. For the three specimens analysed last, the errors estimated for the $^{40}Ar/^{36}Ar$ ratios are 3% or less.

The errors given for the $^{40}K/^{36}Ar$ ratios are based on the estimated relative errors in the measured amounts of potassium and ^{36}Ar, combined in the usual root-mean-square fashion for random errors. This ratio is also sensitive to systematic errors in calibration and in the isotopic abundance of ^{40}K, but the possibility of such errors is not incorporated in the errors listed, which are to be considered as estimates of random error.

The correlation factors listed in the tables are estimates of the degree to which the errors in the $^{40}K/^{36}Ar$ and $^{40}Ar/^{36}Ar$ ratios are correlated. These factors are needed for least-squares fitting of straight lines to the data, according to the method of York (1969). The correlation factor is small when most of the estimated error in the $^{40}K/^{36}Ar$ ratio is associated with error in the potassium measurement and is large (close to unity) when most of the error is associated with measurement of ^{36}Ar.

The last three columns of Tables 3-2 through 3-6 give the amounts of radiogenic argon (denoted in the tables as $^{40}Ar^{*}$) and the apparent ages based on these amounts, calculated on the basis of the assumptions of conventional potassium-argon dating (Dalrymple and Lanphere, 1969, pp. 50-51). The values used for the decay constants and isotopic abundance of ^{40}K, and for the iso-

topic composition of atmospheric argon, are those adopted by the IUGS Subcommission on Geochronology in 1976 (Steiger and Jäger, 1977). The errors given for the amounts of radiogenic argon and for the apparent ages are based on estimated errors in the argon isotopic measurements and the potassium measurements, combined by formulas that take into account how uncertainty in the amount of radiogenic argon depends non-linearly on the ratio $^{40}Ar/^{36}Ar$ (Cox and Dalrymple, 1967). It is important to note that the uncertainty in amount of radiogenic argon rises very rapidly as the percentage of radiogenic argon becomes small and that the calculated apparent age is meaningless if the measured ratio $^{40}Ar/^{36}Ar$ is not significantly different from the value for atmospheric argon. It must also be emphasized that the values used for the errors of measurement are estimates, based on experience but not precisely known. (There are not enough data to establish a level of confidence for these estimated errors, and a high level of confidence is not intended. Rather, the estimates are intended to correspond to the standard deviation of a normal error distribution.) Hence, the errors given for the apparent ages, calculated from these more fundamental error estimates, should be considered to be only rather crude indicators of the uncertainty in each age value due to random analytical error. In this work, some of the apparent ages are much less reliable (analytically) than others, and this is indicated clearly by the wide range in error values given in the tables.

At the bottom of the table of data for each specimen is a set of data obtained by combining all of the data for the different dissolution steps. Also given in most cases are data obtained by combining the data from certain selected dissolution steps. The reasons for these selections are given in the discussion of results from the individual specimens in the following section. The order in which the individual specimens are discussed is not the chronological order in which the specimens were analysed, but rather is based on the degree of correlation between the ratios $^{40}Ar/^{36}Ar$ and $^{40}K/^{36}Ar$ for each specimen. This order of discussion has been chosen because of the increasing complexity of the interpretation required as the degree of correlation decreases.

3.3.4 Potassium-Argon Isotope Correlations

The $^{40}Ar/^{36}Ar$ and $^{40}K/^{36}Ar$ ratios were used to construct an isotope correlation diagram for each specimen. In each case a best-fitting line was determined by use of the formulas given by York (1969) for least-squares fitting of a straight line with correlated errors. The data were weighted inversely as the square of the errors given in Tables 3-2 through 3-6, and the correlation factors given in these tables were used in the computations. Approximate values for the standard errors in the slope and the intercept were also computed, by use of York's (1969) equations 11 and 12.

Figure 3-2 is the isotope correlation diagram for SDS-8. Only four points are plotted as solid points because the solution that was to have been used for potassium measurement for the second step was contaminated. These data show a high degree of correlation, and the deviations of the points from the best-fitting straight line, which has been drawn on the figure, are well within the ranges of estimated analytical error, shown as error bars on the diagram. The slope of the best-fitting line corresponds to an age of 271 million years (Ma) and the $^{40}Ar/^{36}Ar$ intercept is 293. The approximate error in the slope corresponds to 31 Ma, and the approximate error in the intercept is 4. It is not likely that having the missing potassium content of the salt dissolved in the second step would make much difference in interpretation of the results. If that salt had a potassium content (and a relative error for the potassium measurement) similar to that observed for the salt dissolved in the steps immediately preceding and immediately following it (as suggested by values given in brackets in Table 3-5), then the best-fitting line would have a slope corresponding to an age of 279 Ma and an intercept of 291. (The open circle on the figure shows where the point for step 2 would lie if the potassium content of the salt dissolved in step 2 had been 86 mg/kg.) The slope and the intercept of this line do not differ significantly from those of the line determined from the four solid points.

The data for SDS-9 are also well correlated, in the sense that none of the points deviates from the best-fitting line by more than estimated error (Figure 3-3). Because of the low range of values for the $^{40}K/^{36}Ar$ ratio in this specimen, there is a corresponding small range in the $^{40}Ar/^{36}Ar$ values and the analytical errors for this coordinate are quite large on the scale of this figure. The slope of the best-fitting line corresponds to an age of

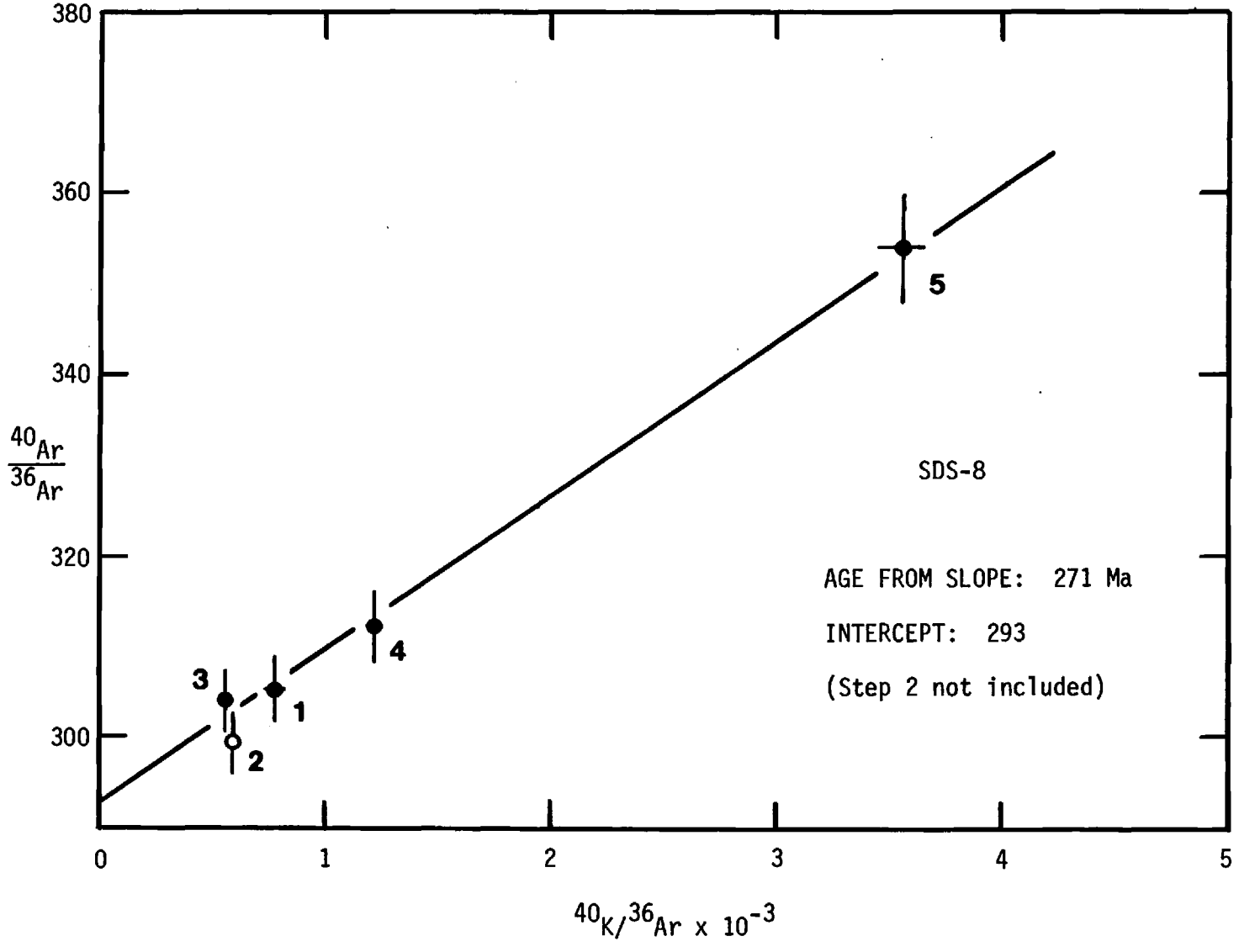

Figure 3-2. Isotope Correlation Diagram for SDS-8

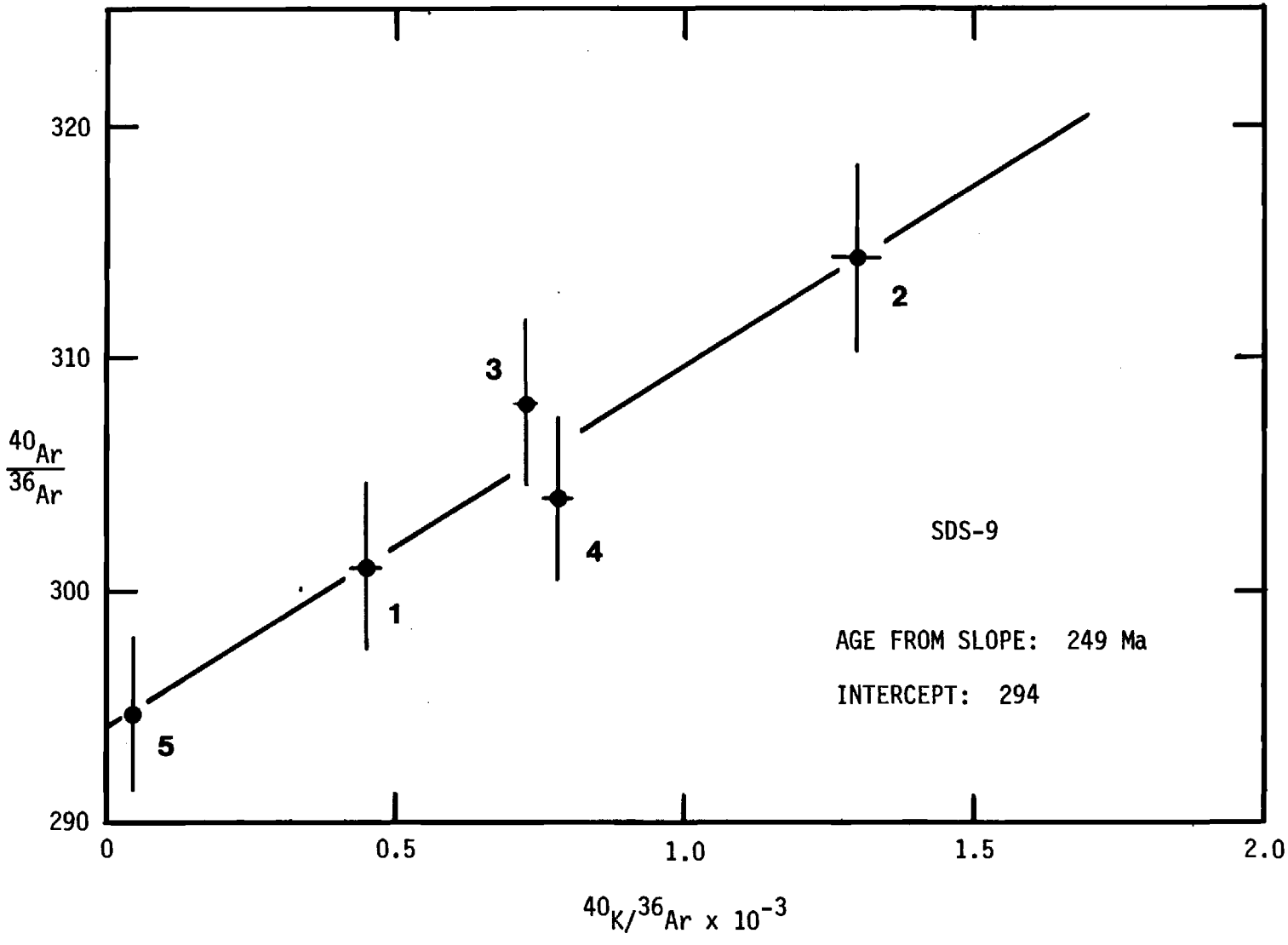

Figure 3-3. Isotope Correlation Diagram for SDS-9

249 Ma with a large error corresponding to about 59 Ma. The intercept is 294 and has an approximate error of 6. The $^{40}Ar/^{36}Ar$ intercepts of the best-fitting lines for SDS-8 and SDS-9, the two specimens from the 792.6-m level of the Grabbe #1 well, are indistinguishable from one another and from the $^{40}Ar/^{36}Ar$ ratio of modern atmospheric argon. The slopes of these lines are not defined precisely, because both specimens have relatively low $^{40}K/^{36}Ar$ ratios, and the difference in their slopes, although relatively large, is not significant.

Figure 3-4 is a diagram of the data for SDS-7. The ratios for this specimen have generally much greater values than those for SDS-8 and SDS-9, and the estimated errors are comparable to the size of the points plotted, except in one case. The best-fitting line, which is shown as a solid line on the figure, has a slope corresponding to an age of 280 Ma and an intercept of 270. The approximate error in the intercept is 2 and the approximate error in the slope corresponds to 9 Ma. Although the correlation of these data is evidently strong, it may be noted that three of the five points are only in grazing contact (error bars considered) with the best-fitting line. Since there is a possibility that some of the potassium from the large fluid inclusion that opened in step 2 was carried over into step 3 (Section 3.3.2, above), and since the deviation of the points for steps 2 and 3 are in the senses one would expect if such a carry-over of potassium had occurred, an alternative line fitting has been done with the data from steps 2 and 3 combined. The open circle on the diagram is for steps 2 and 3 combined, and the dashed line is the line that best fits the set of four points comprising this point and those for steps 1, 4, and 5. The slope of this line corresponds to an age of 262 Ma (approximate error 10 Ma) and the intercept is 280 (approximate error 2). All four points involved fit this line very well.

The data for the first two specimens analysed do not have the high degree of correlation shown by the data from SDS-7, -8, and -9. Figure 3-5 presents the data from SDS-6. The best-fitting line for these data (shown as a solid line on the figure) has a slope corresponding to an age of 145 Ma (approximate error 18 Ma) and an intercept of 334 (approximate error 4). The scatter of the data about this line far exceeds the uncertainty in the data. This situation would not be much improved if one were to discount the data from steps 1 and 6, in which very little of the specimen was dissolved and which may have included some superficial atmospheric argon contamination. Since the potas-

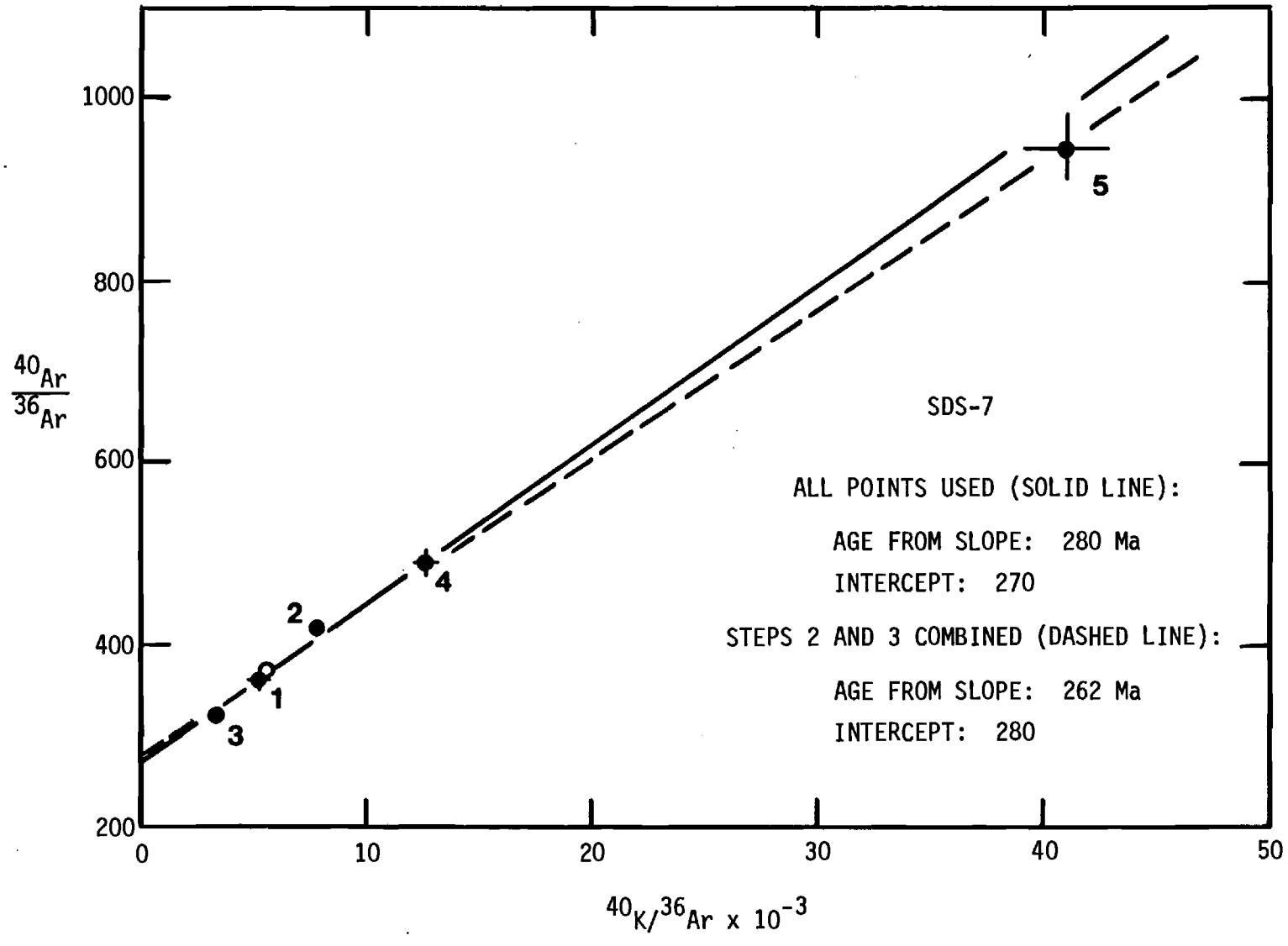

Figure 3-4. Isotope Correlation Diagram for SDS-7

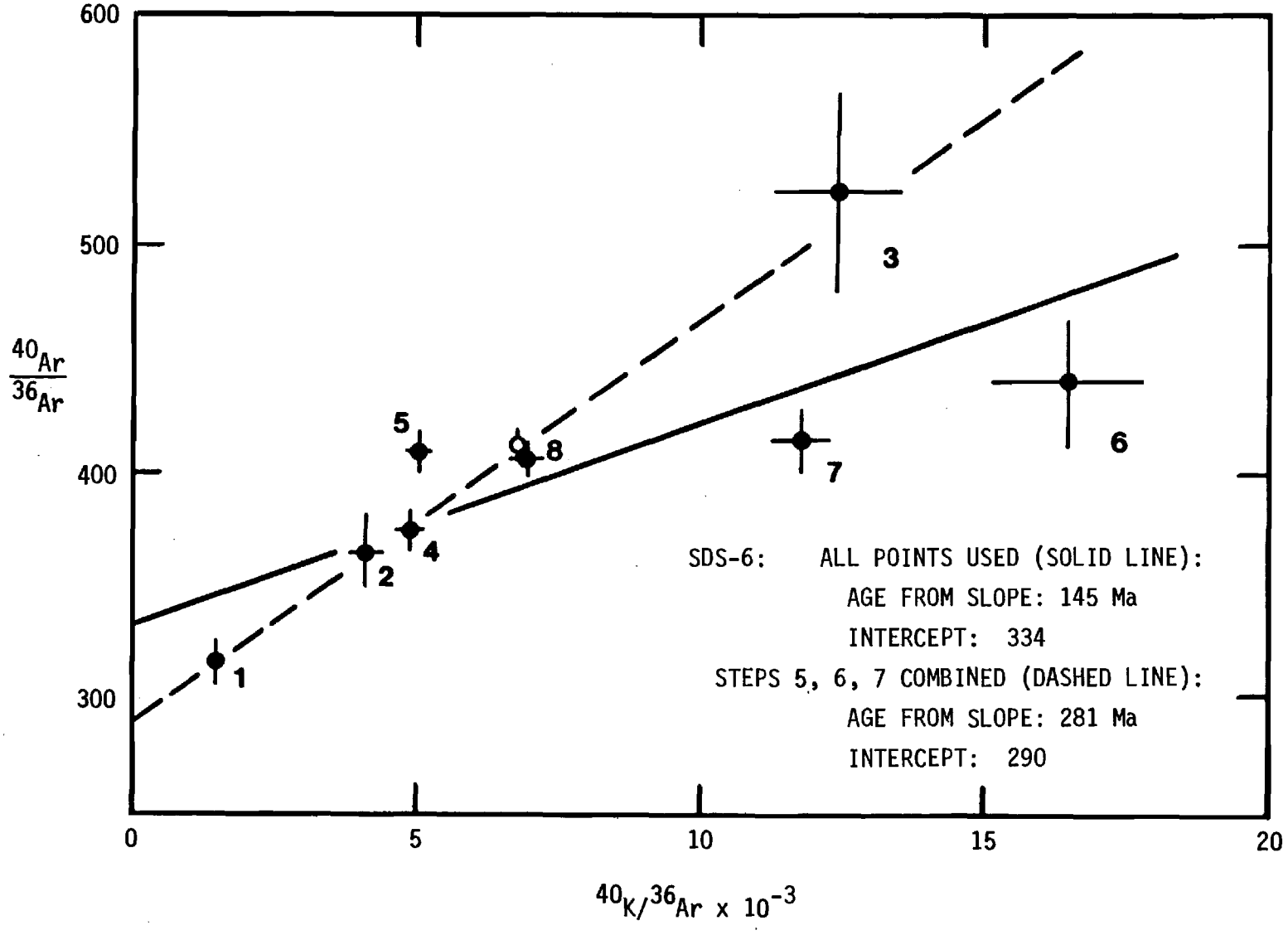

Figure 3-5. Isotope Correlation Diagram for SDS-6

sium analyses suggest that some potassium from the largest fluid inclusion in this specimen was carried over into steps 6 and 7, after the inclusion opened in step 5, it is reasonable to consider the set of data after combining the data from steps 5, 6, and 7. Such a combination, shown as an open circle on the diagram, produces a remarkable improvement in the degree of correlation, and the (dashed) line that best fits the new set of data has parameters that are much more like the best-fitting lines found for the other specimens, a slope corresponding to an age of 281 Ma and an intercept of 290. The approximate error in the slope of the six-point line corresponds to 24 Ma, and the approximate error in the intercept is 6.

The estimated analytical errors for the first specimen analysed, SDS-5, are greater than for the other specimens, partly because of the experimental nature of the work with the first specimen and partly because the mass spectrometer was becoming unstable as failure of its filament was approaching. Figure 3-6 shows the data for this specimen. The line that best fits these data, shown as a solid line on the figure, has a slope corresponding to an age of 226 Ma (approximate error 28 Ma) and an intercept of 300 (approximate error 9). As in the case of SDS-6, the deviations of some of the points from this line are greater than the estimated errors. Since the largest fluid inclusion in SDS-5 opened during the third step, it is interesting to see the effect of combining the data for steps 3 and 4, even though there is no indication from the potassium data that potassium may have been carried over from step 3 into step 4. When these steps are combined, as shown by an open circle on the diagram, the best-fitting line has a slope corresponding to an age of 261 Ma (approximate error 35 Ma) and an intercept of 294 (approximate error 11). This line is shown as a dashed line on Figure 3-6. Although the parameters of this line are consistent with those of the best-fitting lines obtained for the other specimens (after combining data points in some cases), two of the four points are well off the line. There is no way to determine whether the relatively poor correlation of the data for this specimen is a consequence of something in the history of the specimen before it was analysed or is a consequence of analytical errors that exceed the error estimates. The circumstances under which this specimen was analysed make the latter possibility seem rather probable, however.

The procedure of combining data from steps where large fluid inclusions opened with data from one or more subsequent steps, on the assumption that

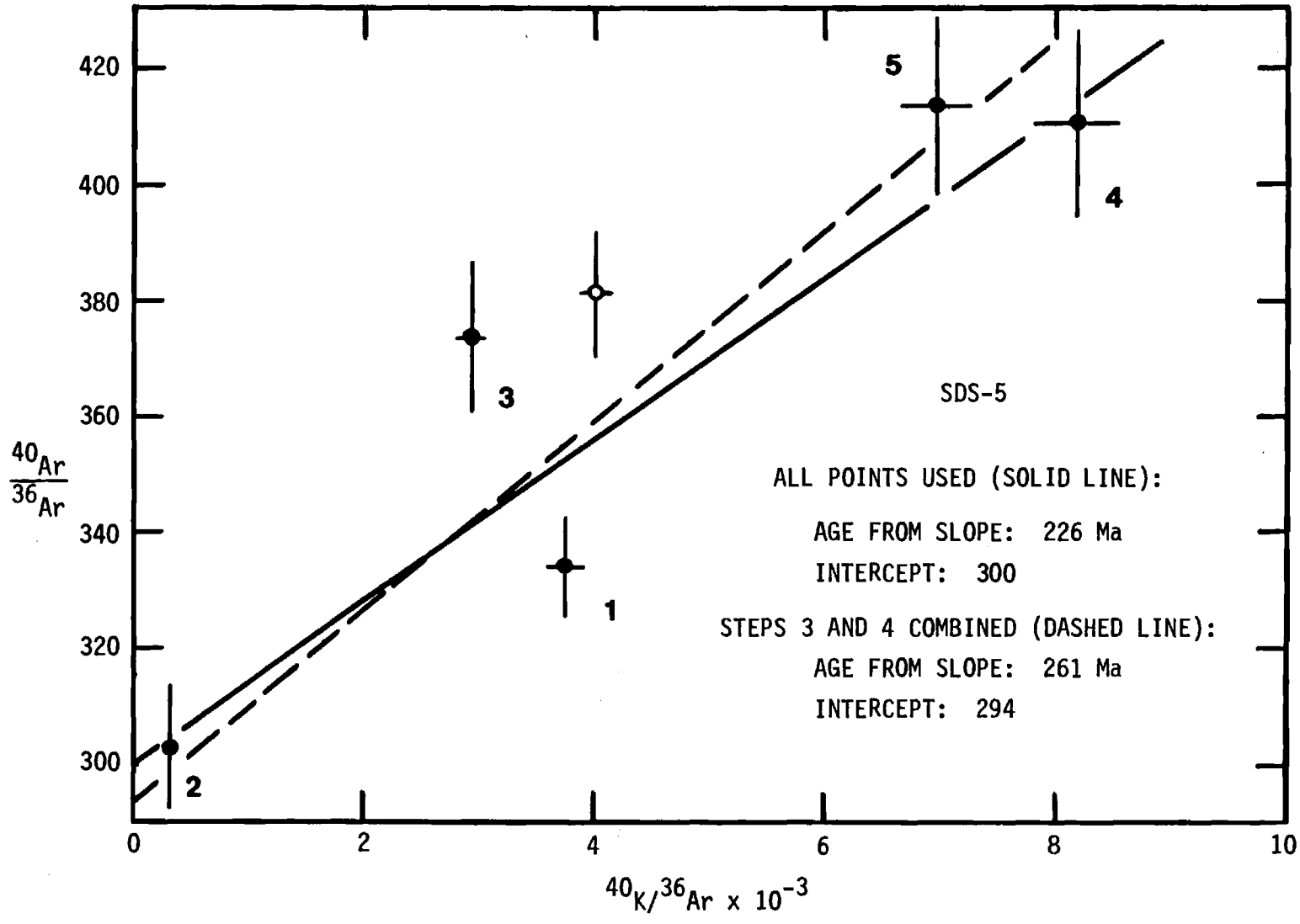

Figure 3-6. Isotope Correlation Diagram for SDS-5

some potassium from the inclusions was carried over into the following step(s), appears to be justifiable not only from evidence obtained from the individual specimens (that is, the elevated potassium levels observed in steps following the opening of inclusions and the improved correlation of the data for individual specimens when data are so combined) but also because it brings the parameters of all the best-fitting lines into reasonable agreement. The best-fitting lines obtained after combining data in this way all have slopes corresponding to ages in the range 249 Ma to 281 Ma, and the approximate errors calculated for these slopes are such that the error ranges for all of them overlap in the range of slopes corresponding to 257 Ma to 272 Ma. All of the intercepts are in the range 280 to 294. All but one of the intercepts are within the calculated approximate error of the $^{40}Ar/^{36}Ar$ ratio of modern atmospheric argon.

Because four of the five intercepts do not differ significantly from the $^{40}Ar/^{36}Ar$ ratio of modern atmospheric argon, there is no need to be concerned about the possible influence of contamination of the specimens with atmospheric argon during their preparation. Therefore, the data from the first step in dissolution of each specimen have been included in computation of the best-fitting line for the specimen, even though these data may have been affected by some atmospheric argon recently acquired by the specimen. In the one case (SDS-7) where the intercept of the best-fitting line differs from the $^{40}Ar/^{36}Ar$ ratio of modern atmospheric argon, the amount of ^{36}Ar released in several steps was small enough that uncertainty about the role of contamination by modern atmospheric argon is of little importance in respect to the slope of the isotope correlation line.

3.3.5 Results Obtained by Crushing Specimens in Vacuum

The data obtained in experiments in which six specimens having fluid inclusions were crushed in vacuum are presented in Table 3-7. The data are given in the order in which the experiments were carried out. The first specimen crushed, from a depth of 792.4 m, had a few millimeter-sized fluid inclusions. In the first crushing experiment, the amount of argon released was so great that it far exceeded the measurement range of the mass spectrometer. Special procedures were used to reduce the amount of argon to a measureable level, but these may have caused some isotopic fractionation of argon within

Table 3-7. Data From Fluid-Inclusion-Bearing Specimens Crushed in Vacuum

Depth[a] Specimen	Potassium Recovered[b] (μg)	$^{40}Ar/^{36}Ar$	^{40}Ar (pmol)	$^{40}Ar^*/^{40}Ar$ (%)	$^{40}Ar^*$ (pmol)	Calculated Age[b] (Ma)
792.4 m						
1	213	292	5500	-	-	-
		295	181	0.0	-	-
2		296	52	0.1	0.05	
3		304	3.9	2.8	0.12	
764.9 m						
1	64	332	165	11.0	18.2	1170
B2	15	305	167	3.0	5.0	1310
A2	12	406	7.3	27.2	2.0	770

(a) All of these specimens were from the Grabbe #1 well.

(b) It is probable that not all of the potassium from the fluid inclusions was recovered. The age values are based on the amounts of potassium recovered and are probably larger than the apparent ages that would have been obtained if there had been a way to ensure complete recovery of the potassium.

the apparatus. So the fact that the $^{40}Ar/^{36}Ar$ ratio measured is slightly below that of atmospheric argon is not likely to be significant. Although the large amount of argon is presumed to have come from the specimen, it is possible that argon was released from the crushing apparatus as a consequence of mechanical strain during the crushing procedure. The specimen was further crushed and the much smaller amount of argon so released was found to be isotopically identical to atmospheric argon. Afterward the crushed material was soaked in absolute ethanol in an attempt to extract the potassium that had been in the fluid inclusions. About 150 mg of salt was dissolved in the ethanol, of which 213 μg was potassium.

Two other specimens from the 792.4-m level were crushed. These specimens were selected because they had only very small fluid inclusions, so that the mass spectrometer would not be overwhelmed with argon. The amounts of argon released by crushing these specimens were well within the range of the instrument. One released 52 pmol of argon with an isotopic composition like that of atmospheric argon. The other released only 3.9 pmol of argon, which was slightly enriched in ^{40}Ar.

Three specimens from a depth of 764.9 m were selected for crushing. These each contained a fluid inclusion with dimensions of the order of a millimeter. In each case, the argon released was enriched in ^{40}Ar, the maximum enrichment corresponding to 27% radiogenic argon. Ethanol was used in an attempt to extract the potassium from the inclusions opened in these crushing experiments. The amounts of salt dissolved in the ethanol were in the range 63 to 83 mg, and the potassium contents as indicated in Table 3-7 range from 12 to 64 μg. Calculated ages based on the amounts of potassium recovered are several times greater than the ages associated with the best-fitting isotope correlation lines from the stepwise dissolution experiments. The large age values are likely a consequence of incomplete extraction of potassium by the ethanol.

These crushing experiments were done before the stepwise dissolution work, and they were viewed as preliminary experiments intended to show the typical amount of argon in the fluid inclusions and to identify portions of the core sections where some radiogenic argon is present in fluid inclusions. There is no obvious way to obtain accurate potassium-argon ages from the fluids released in such crushing experiments, short of working with very large inclusions in an apparatus specially designed for such work.

Given the uncertainty in the effectiveness of the potassium recovery and some uncertainty about the source of the argon released during crushing, the data obtained are consistent with the data from the stepwise dissolution work. The points of agreement are as follows:

(1) Millimeter-sized fluid inclusions contain relatively large amounts of potassium, 10 μg or more.

(2) Radiogenic argon is present in millimeter-sized inclusions in sufficient quantities to yield apparent ages of hundreds of millions of years.

(3) Salt from about 793 m deep in the Grabbe #1 well contains more atmospheric argon than salt from about 765 m deep, and has correspondingly smaller proportions of radiogenic argon.

3.4 DISCUSSION

According to a current geological time scale (Harland et al., 1982), the rock salt of the lowermost Upper Permian, San Andres Formation should be about 255 million years old. But, owing to the ease with which salt recrystallizes, the age of the halite crystals will not necessarily correspond to the age of the rock. Roedder (1984) has presented petrographic criteria that may be used to identify primary bedded salt, that is, salt that has retained the original halite crystals that formed in the original evaporite environment. The primary salt contains an abundance of minute fluid inclusions in a characteristic chevron pattern. According to Roedder, much bedded salt does not show the characteristics of primary salt, but instead consists of clear, relatively equant crystals that show clear evidence of having formed largely by recrystallization. (They may include some small portions of the primary salt.) It is in such crystals that the larger, millimeter-sized fluid inclusions may be found.

The salt specimens chosen for the present study were selected with several criteria in mind, none of which favored the selection of primary salt crystals. For the most part, specimens were selected to be as free as possible of fractures and complex grain boundaries where relatively large amounts of atmospheric argon might occur. Thus, fragments of single crystals were preferred over multicrystalline specimens. Clear salt was preferred over clouded salt, so that fractures and fluid inclusions could be seen well, and three

specimens were specifically chosen because they had millimeter-sized fluid inclusions. Thus there was a deliberate bias in the sampling toward selection of specimens that consisted of recrystallized salt, but the bias was a consequence of the need to use favorable specimens in establishing a heretofore untried analytical procedure rather than a choice based on the geological significance of the specimens. However, in respect to the siting of a nuclear-waste repository, the age of recrystallized salt is presumably of more interest than the age of primary crystals.

The data obtained by stepwise dissolution of these five salt specimens are, if the data from certain steps are combined as described above, generally well correlated, having best-fitting lines with slopes that correspond to ages in the range 249-281 Ma and intercepts in the range 280-294. An obvious interpretation of these data is that the best-fitting lines correspond approximately to the isochrons that would be expected for salt specimens that formed in Permian time with initial argon of atmospheric composition and have since remained undisturbed. The ratio $^{40}Ar/^{36}Ar$ in the Permian atmosphere should have been smaller than that in the modern atmosphere, but models for degassing of the earth (Ozima, 1975) indicate that the difference should be quite small. In such an interpretation, the range in slopes and intercepts can be attributed entirely to the effects of the relatively large analytical errors. For the specimens to yield such "internal" isochrons requires that potassium and argon have remained fixed within the specimens on a scale of millimeters (that is, the scale on which different portions of the specimens were separated in the process of stepwise dissolution) for most of the 255 million years since the rock was deposited.

Because of the relatively large analytical errors in this work, and because the errors are only estimates of standard deviations of the measurements (which cannot be determined directly in this sort of work), it would not be gainful to attempt an elaborate statistical analysis of the data to try to establish the significance of the best-fitting lines as isochrons. But, following a suggestion by Brooks et al. (1972), the standard errors for the slopes and intercepts of the lines can be computed in the two different ways given by York. The first method proposed by York (1966), referred to by Brooks et al. as the "York 1" method, provides calculated uncertainties for the slope and intercept of a best-fitting line that are influenced by the scatter of data points about the fitted line. The second method, called the

"York 2" method, is that used in the preceding section to calculate approximate standard errors for slopes and intercepts with formulas that consider the errors of measurement but not the scatter of points about the fitted line. Comparison of the errors calculated in these two different ways indicates whether or not the data points are scattered more than would be expected as a result of analytical error alone (Brooks et al., 1972) and thus can indicate situations where best-fitting lines cannot be valid as isochrons.

Table 3-8 provides a summary of the parameters of the best-fitting lines, and the associated approximate errors, calculated by the "York 2" method and presented in the preceding section. The table also includes a listing of parameters and associated errors for best-fitting line calculated from the same data by the "York 1" method. (The "York 1" method does not permit use of the error correlation factors, but the differences in the line parameters found by the two different methods are generally quite small.) The errors calculated by the "York 1" method are notably greater than those calculated by the "York 2" method for the best-fitting lines for SDS-5, SDS-6, and SDS-7 in the cases where all data points are used. The same is true for SDS-5 when data from steps 3 and 4 are combined, but when selected steps are combined for SDS-6 and SDS-7 the "York 1" errors are smaller than the "York 2" errors. "York 1" errors are also smaller than "York 2" errors in the cases of SDS-8 and SDS-9. The significance of these comparisons is considered in the following paragraphs. (For the purpose of this part of the discussion, it will be assumed that any scatter of data in excess of what may be attributed to analytical error or artifacts is due to failure of a specimen to have behaved as a closed system internally. The possibility of isotopic inhomogeneity of the initial argon in the specimen will not be considered until later in the discussion.)

Neither of the two lines calculated for SDS-5 can be considered to be an isochron. Unless the analytical errors for the analysis of this specimen have been considerably underestimated (which is possible in this particular case), the specimen has not been a closed system internally and the best estimate of the age of the specimen from these potassium-argon data is the conventional apparent age calculated from a combination of the data from all of the steps, 282 ± 43 Ma.

The best-fitting lines based on all of the data obtained for SDS-6 and SDS-7 cannot be considered to be isochrons. Either these specimens have not

Table 3-8. Potassium-Argon Isotope Correlation Lines Obtained by Least-Squares Fitting

Specimen	Data Set	"York 2" Method[a] Age (Ma)	"York 2" Method[a] Intercept	"York 1" Method[b] Age (Ma)	"York 1" Method[b] Intercept
SDS-5	5 points	226 ± 28	300 ± 9	232 ± 63	299 ± 18
	4 points (Steps 3 and 4 combined)	261 ± 35	294 ± 11	263 ± 86	293 ± 22
SDS-6	8 points	145 ± 18	334 ± 4	173 ± 48	325 ± 19
	6 points (Steps 5-7 combined)	281 ± 24	290 ± 6	277 ± 12	291 ± 4
SDS-7	5 points	280 ± 9	270 ± 2	290 ± 20	266 ± 9
	4 points (Steps 2 and 3 combined)	262 ± 10	280 ± 2	263 ± 6	279 ± 3
SDS-8	4 points (Step 2 omitted)	271 ± 31	293 ± 4	270 ± 15	293 ± 2
SDS-9	5 points	249 ± 59	294 ± 6	249 ± 34	294 ± 2

(a) York's (1969) method for least-squares fitting of a straight line with correlated errors. The calculation of errors does not take into account the scatter of data points about the fitted line (Brooks et al., 1972).

(b) York's (1966) method for least-squares fitting of a straight line. Calculated errors are influenced by the scatter of data points about the fitted line.

been closed systems internally, or the analytical procedure was inadequate in respect to the carry-over of potassium from one step to the next after the large fluid inclusions in these specimens opened. As noted in Section 3.2.1, there is always some carry-over of potassium from one step to the next, but the effect should be minimal when potassium is uniformly distributed in the salt. The probability that significant amounts of potassium were carried over after large fluid inclusions opened, in these particular cases, was enhanced by the high potassium content of the fluids (relative to halite) and by the fact that dissolution steps were terminated just after the inclusions opened. If the hypothesis of carry-over of potassium is accepted as justification for combining those steps in which abnormally high potassium levels were observed, then the best-fitting lines so obtained could be considered to be isochrons. In the case of SDS-6, the age of 281 $\pm$ 24 Ma and the intercept of 290 $\pm$ 6 are acceptable (but not very persuasive) as the parameters of an isochron for mid-Permian salt. The conventional potassium-argon age for all the data combined, 267 $\pm$ 9 Ma, indicates that the specimen as a whole has probably behaved as a closed system since it was formed. The best-fitting line for SDS-7, when steps 2 and 3 are combined, has a slope that is acceptable for a mid-Permian isochron, corresponding to 262 $\pm$ 10 Ma, but the intercept of 280 $\pm$ 2 is low. The conventional apparent age for the whole specimen in this case is 227 $\pm$ 6 Ma, which shows that either the specimen is notably younger than the mid-Permian rock from which it came, or that the specimen has not been a completely closed system. Disregarding the small amount of salt dissolved from the specimen in the first step, the apparent ages for the individual steps cluster around 250 Ma except for step 3, which has a substantial deficit of radiogenic argon. (If potassium was carried over from step 2 to step 3, then the deficit in radiogenic argon is shared by these two steps.) It is reasonable to suspect that the unusually large fluid inclusion in this specimen has been involved in migration of argon and perhaps potassium in a way that has not affected the entire crystal.

Specimens SDS-8 and SDS-9 both have best-fitting lines that may be considered to be isochrons. The slopes are not well determined, because non-radiogenic argon is so abundant in these specimens that the variability in $^{40}Ar/^{36}Ar$ is small. The corresponding ages, 271 $\pm$ 31 Ma and 249 $\pm$ 59 Ma, are reasonable for mid-Permian salt, but obviously they do not place close constraints on the ages of the specimens. The intercepts are relatively well

determined as 293 ± 4 and 294 ± 6 and are quite consistent with the idea that they represent the isotopic composition of (Permian) atmospheric argon. The conventional apparent age for SDS-8 (necessarily excluding step 2) is 239 ± 31 Ma, a result not inconsistent with the 271 ± 31 Ma age based on the slope of the best-fitting line. The conventional apparent age for SDS-9 is not useful, because it has been profoundly affected by the large amount of presumably atmospheric argon released in step 5. A very slight difference (well within the range of analytical error) between the $^{40}Ar/^{36}Ar$ ratio determined for this step and that of atmospheric argon has caused a large negative age value to be calculated for step 5 and makes the age calculated for the whole specimen meaningless. (This particular case shows an advantage of the stepwise dissolution method for potassium-argon analysis of salt, relative to analysis of whole specimens, that is independent of whether or not the stepwise analysis actually results in a valid internal isochron.) The apparent ages for steps 2 and 3 are appropriate for Permian salt, but they too are rather imprecise.

In summary of the interpretation of the best-fitting isotope correlation lines, it is clear that some of the specimens have not behaved internally as closed systems. There is no isochron for SDS-5. Although data from SDS-7 appear to fit a straight line well, there is clear evidence that this specimen cannot have been a closed system since mid-Permian time, internally or as a whole. If the supposed carry-over of potassium from step 5 to steps 6 and 7 for SDS-6 is sufficient reason to combine these steps, then the data provide a line that may be an internal isochron for this specimen. But the line is not very well determined, nor are the isotope correlation lines for SDS-8 and SDS-9, which may be isochrons, well determined. In spite of all the uncertainty in the accuracy of the data and about the validity of the possible interpretations, there is some quite useful information provided by these data. Those correlation lines that may be isochrons are mutually consistent with one another, they are consistent with most of the conventional potassium-argon ages calculated for the specimens, and they show rather clearly that these salt specimens have behaved <u>largely</u> as closed systems, even internally, since the close of the Paleozoic Era. In the cases of two of three specimens having millimeter-sized fluid inclusions, the whole specimens appear to have behaved as closed systems since mid-Permian time, even though there may well have been internal migration of argon and potassium near these inclusions.

The combined data for steps 5-7 of SDS-6 give a potassium argon apparent age of 273 $\pm$ 12 Ma, and the point for the combined data correlates with the rest of the data for the specimen on the isotope correlation diagram. It may be concluded that the fluid inclusion and the salt around it (all of the salt dissolved in steps 5-7) behaved as a closed system since mid-Permian time. Whether or not there may have been some interchange of potassium and argon between the inclusion and the salt immediately surrounding it cannot be determined, given the probable carry-over of some potassium from step 5 into the subsequent steps. If the carry-over hypothesis is not valid, then some radiogenic argon has found its way from the surrounding salt into the inclusion, leaving behind the potassium from which it had been formed, since the apparent age for the step in which the inclusion opened is 353 $\pm$ 20 Ma and the apparent ages for the two subsequent steps are correspondingly low. The distance over which argon and potassium associated with the large fluid inclusion in SDS-5 could have moved is apparently larger, but at least the whole specimen appears to have been a closed system. Even in the case of SDS-7, where there is a definite indication of some loss of radiogenic argon from a very large fluid inclusion, or from salt near it, the deficit of radiogenic argon is small enough that it appears likely that the loss of argon occurred early in the history of the rock. Overall, the data related to the millimeter-sized fluid inclusions indicate that these inclusions have not moved appreciably within the salt since the end of the Paleozoic Era.

For each of the specimens, the relatively large range of values for the ratio $^{40}K/^{36}Ar$ is due mostly to variability in the amount of ^{36}Ar released per unit mass of salt dissolved rather than to variability in the potassium content of the salt. The variability in amount of ^{36}Ar is not surprising, given the non-uniform distribution of small fluid inclusions noted for most of the specimens. An important question is whether the ^{36}Ar is largely from the modern atmosphere or from the Permian atmosphere, or possibly from argon incorporated at some intermediate time. Since the Permian atmosphere is not expected to have had a $^{40}Ar/^{36}Ar$ ratio much different from that of the modern atmosphere, and since the intercepts of the best-fitting lines obtained in this work do not differ significantly from the ratio for the modern atmosphere (except in the one case, SDS-7, where there is a definite indication of some loss of radiogenic argon), the isotopic data do not provide a direct answer to this question. But consideration of the $^{40}K/^{36}Ar$ ratio as a function of step

number and of the general correlation of radiogenic argon and potassium released in the dissolution steps suggests an indirect answer.

If most of the ^{36}Ar in the specimens had been from atmospheric contamination introduced artificially (at any time since the drilling began), one would expect that the influence of such argon would be greatest in the first step of dissolution and progressively less in the later steps. Perusal of the step numbers on the figures suggests that there may be such a pattern -- the first step is usually among the leftmost points on the graphs and the last two steps are usually (three out of five cases) the rightmost points. But the step in which the most ^{36}Ar (relative to potassium) was released was the first step in only one case (SDS-6), and in one important case (SDS-9) the amount of ^{36}Ar released in the last step was much greater than in any of the other steps. In this particular case the unusually large amount of ^{36}Ar appears to have been associated with a portion of the specimen that was exceptionally rich in mineralogical impurities, an association that is not hard to understand if the ^{36}Ar is from argon that was trapped as the halite crystal grew over the impurities.

The points plotted for the steps in which large fluid inclusions opened (known with reasonable certainty only for specimens SDS-5, -6, and -7) have intermediate $^{40}K/^{36}Ar$ ratios but they are well to the left of at least one other point in each case. It is clear that ^{36}Ar is concentrated in the fluid inclusions relative to some portions of the salt, and for those inclusions for which a high potassium content is evident (in SDS-6 and SDS-7) the relative concentration of ^{36}Ar is quite large. Such enrichment would be expected if the inclusions formed from a fluid that had been in equilibrium with air, or with a subsurface gas mixture that included a lot of air, before these salt crystals formed.

It seems evident that much of the ^{36}Ar in these specimens was deep within the specimens rather than preferentially near the outer surfaces as one might expect if artificial contamination (for example, by way of temporarily opened fractures) were a major factor. Relatively large amounts of ^{36}Ar appear to have been associated with mineral impurities and with fluid inclusions, as one would expect if such argon had been trapped within the halite crystals as they grew. The good correlation between radiogenic argon and potassium, on a scale of millimeters within these crystals (including the large fluid inclusions), implies that the specimens have in large part been closed systems for roughly

250 million years but does not rule out the possibility that extraneous argon has permeated the salt more recently along restricted pathways, for example along grain boundaries. But the specimen which had the largest amount of ^{36}Ar, SDS-9, was a fragment of a single crystal having no boundary between large crystals; so was SDS-5, which released an unusually large amount of ^{36}Ar during the second step of its dissolution. The specimens that were composites of more than one crystal, SDS-6 and SDS-8, each gave $^{40}K/^{36}Ar$ ratios that are generally comparable to the other specimen(s) from the same depth, so there is no indication of a concentration of ^{36}Ar along the boundaries between the (large) crystals. The weight of the evidence is in favor of the idea that most of the extraneous (that is, non-radiogenic) argon in these specimens was trapped early in the history of the rock during a period of extensive recrystallization of the halite.

If the extraneous argon within these salt specimens was largely argon that had been trapped when the crystals formed, then the amounts of such argon should provide information about the environment(s) in which the crystals grew. The only case where the amount of argon from a fluid inclusion and the volume of the inclusion are known with fair accuracy is the case of the large fluid inclusion within SDS-7, which opened during the second step of dissolution of that specimen. The amount of ^{36}Ar released in that step was 40 fmol; if that amount of ^{36}Ar had been originally dissolved in 3 mm^3 (the approximate volume of the fluid inclusion) of brine, then there is good reason to believe that the brine that was trapped had been in equilibrium with air as a brine, rather than having been fresh water in which salt was dissolved after its last equilibration with air. The observed concentration is 13 pmol [30 x 10^{-8} cm^3 (STP)] of ^{36}Ar per cm^3 of fluid, an amount quite closely comparable to that found in several deep brines from the Palo Duro Basin by Zaikowski et al. (1987) and interpreted by them to be waters that were brines when they were last in equilibrium with the atmosphere. (It should be noted, however, that this fluid inclusion may have lost some radiogenic argon at some time after it formed, as suggested above, so it could also have lost some of its original atmospheric argon.)

If the 1-mm long fluid inclusion in SDS-5 opened during the third step of dissolution of that specimen, then its ^{36}Ar content was not more than 11 fmol, corresponding to a concentration similar to that in the large fluid inclusion in SDS-7. The amount of ^{36}Ar released from SDS-6 during the fifth step of its

dissolution was 21 fmol. If the volume of the fluid inclusion that opened during this step has been underestimated, as suggested earlier (Section 3.3.2) because of the relatively large amount of potassium released in the step, then the concentration of ^{36}Ar in this fluid may not have been much greater than that in the large inclusion of SDS-7, but if the volume estimate is reasonably accurate, then the concentration of ^{36}Ar in this fluid may have been an order of magnitude greater than in the fluid from SDS-7. Such a possibility could be accomodated by postulating that the fluid was fresh water when it last equilibrated with air, or that some air was trapped with the liquid. (If the somewhat smaller fluid inclusion that was nearby opened during the sixth step, the concentration of argon in the largest inclusion would have been somewhat smaller than the calculated value.)

Larger amounts of ^{36}Ar, from 98 to 161 fmol, were released in step 2 in the dissolution of SDS-5, steps 2, 3, and 4 in the dissolution of SDS-8, and steps 3 and 4 in dissolution of SDS-9. In the final step for SDS-9, the amount was much greater, 1630 fmol. None of these steps is associated with the opening of a millimeter-sized fluid inclusion, and these amounts of ^{36}Ar are much greater than the amounts that could have been dissolved in any liquid released during these steps, if the argon had been dissolved in an enviroment where the fugacity of argon was similar to that of argon in the (modern) atmosphere. These relatively large amounts of argon probably represent small volumes of trapped air, or of subsurface gas in which air was a major component. At normal temperature (25°C) and pressure, modern air contains 1290 fmol of ^{36}Ar per mm^3. If air had been trapped in these specimens at atmospheric pressure, then included gas volumes of the order of 0.1 mm^3 must have been fairly common in these specimens, and in the impurity-rich central zone of SDS-9 there must have been a gas volume a little greater than 1 mm^3. Such volumes of void space were not evident during the examination of these specimens before they were dissolved, but it probably should not be expected that such hypothetical gas-filled spaces would have survived during burial of the salt to depths of the order of 1 km. An alternative possibility is that the gas was trapped in an environment having elevated gas pressure. A very large amount of argon, 18 pmol of ^{36}Ar, may have been released from the first specimen that was crushed under vacuum in this work (see Table 3-7). Unfortunately, it is not possible to be sure whether this argon came from the specimen or from the apparatus, which was being used for the first time after having been

assembled. If the argon (equivalent to that in 14 mm^3 of air at normal temperature and pressure) came from the specimen, then it is reasonable to suspect that it may have been trapped under a considerably elevated pressure.

Zaikowski et al. (1987) found that the argon in deep brines from the Palo Duro Basin is enriched in ^{40}Ar relative to atmospheric argon, a consequence largely of water-rock interactions that have released radiogenic argon from potassium-bearing minerals into the groundwater rather than of decay of potassium dissolved in the water. In many cases the $^{40}Ar/^{36}Ar$ ratio in the deep brines is greater than the largest such ratio observed in any of the five salt specimens studied in this work. If these salt specimens formed by recrystallization in an environment in which there was an appreciable enrichment of $^{40}Ar/^{36}Ar$ relative to atmospheric argon, then the potassium-argon ages calculated in the conventional way would be meaningless and the intercepts of the isotope correlation lines should indicate the enhanced $^{40}Ar/^{36}Ar$ ratio of the environment of crystallization. The generally good correlation between $^{40}Ar/^{36}Ar$ and $^{40}K/^{36}Ar$ found in this work (when data from certain steps are combined in some cases), along lines having $^{40}Ar/^{36}Ar$ intercepts that are not higher than the atmospheric ratio, may be used to argue that the formation of these specimens by recrystallization of halite must have occurred relatively early, in an environment in which atmospheric argon was predominant. The significance of this argument is enhanced by the probability that deep brines acquire radiogenic argon early in their history, because there is generally much inherited radiogenic argon present in clastic sediment that could be released by water-rock interactions early in the history of a sedimentary basin.

Although those isotope correlation lines obtained in this work that may be valid as isochrons have intercepts corresponding to the composition of atmospheric argon, the slopes of these lines are greater, except in one case, than that of an isochron for material that formed about 255 Ma ago. None of these slopes is significantly greater than that of a 255-Ma isochron, because the very low potassium content of the salt and the experimental nature of the stepwise dissolution procedure, as it was used in this work, both have contributed to making the estimated relative errors considerably greater than errors in geochronometric work normally are. Nevertheless, if the errors have been conservatively estimated it is a little disturbing to have cases where the presumed age of the rock is near the lower end of the range of uncertainty for

lines that may be isochrons (as for the SDS-6 correlation line based on six points and for SDS-8). The uncertainties in the time scale from which the 255-Ma age for the San Andres Formation was taken are such that the rock may well be at least 260 Ma old, but the possibility that systematic errors are present must also be considered. Some error in calibration is possible, which would have affected the data from all specimens equally. Because a positive correction was made to the amount of argon measured in almost every case, on the basis of a following blank run, and because there is a likelihood that there was some degree of overcorrection in this process in cases where the original amount of ^{36}Ar was rather small, it is possible that the slopes are a little steeper than they should be because of such systematic overcorrection. (The possibility of overcorrection arises because some ^{36}Ar measured in the blank runs may have come from the apparatus.) Of those specimens for which the data may provide valid isochrons, SDS-6 would have been most strongly affected by such an overcorrection, and its (six-point) correlation line has the steepest slope of all.

There is another reasonable explanation of the tendency of the best-fitting lines to be slightly steeper than a 255-Ma isochron. It seems unlikely that this recrystallized rock salt should have formed in a way that meets the criterion of isotopic homogeneity in argon, at the time of closure, to the degree necessary for highly accurate isochrons from rock of very low potassium content. Certainly argon is not distributed homogeneously in the rock, and it seems likely that the rock salt may have been exposed to argon having somewhat different isotopic compositions at different times during the history of deposition and diagenesis. Argon of the Permian atmosphere would have been predominant at the time of initial crystallization of the salt, and the data show that atmospheric argon must have been predominant during the recrystallization that produced these particular specimens. But argon with a significant radiogenic component may have been migrating through the rock before diagenesis was complete. Such argon may have been derived locally by alteration of detrital biotite in the highly saline environment or of other potassium-bearing minerals in the mudstones associated with the salt. If such argon had been trapped in portions of the rock, but did not generally mix with atmospheric argon trapped earlier, it would have a greater effect (on average) on the isotopic composition of argon in those portions of the salt having lesser amounts of atmospheric argon. This could have produced a correlated variation in the

isotope ratios within the rock at the time of closure that would have been in the correct sense to cause the data measured now to fit a line steeper than a correct isochron. To determine whether or not such a possibility is important would require more accurate data, from the analysis of more specimens.

A final note is necessary concerning those specimens, SDS-5 and SDS-7, whose isotope correlation lines are not isochrons. The possibility that brines bearing radiogenic argon may have interacted with these crystals during or after their formation makes any interpretation of their history much less definite than if the environment external to the crystals could be considered to always have been dominated by atmospheric argon. In particular, recent major disturbances cannot be completely ruled out, since recently acquired brine inclusions could not necessarily be distinguished from old ones if the recently acquired inclusions had an intitial radiogenic argon component. But if such recent disturbance has occurred, potassium-argon apparent ages for the disturbed materials that are fairly close to the age of the undisturbed materials could only be obtained fortuitously, and analysis of many specimens should show fairly clearly whether recent interactions between salt and brine could have been important.

In summary, the data obtained in the stepwise dissolution experiments (and in the crushing experiments) are all consistent with the interpretation that the salt and the inclusions contained within the salt formed in Permian time and have been little disturbed since that time. The only disturbances suggested are the possible migration of radiogenic argon from the salt into the fluid inclusions, over distances of a few millimeters (somewhat more, perhaps, in the case of SDS-5), the possible incorporation of relatively small amounts of argon from the modern atmosphere near the surfaces of the specimens, and the loss of some radiogenic argon from within or near the unusually large fluid inclusion in SDS-7. (There is a remote possibility that this large inclusion could have formed recently from a brine containing radiogenic argon.) Although there is considerable uncertainty because of relatively large analytical errors, the slopes of the internal isochrons and many of the conventional apparent ages obtained in this work suggest that the recrystallization that formed these specimens occurred fairly soon (within ten million years or so) after the deposition of the rock. The amounts and the isotopic composition of the argon initially trapped in these specimens are consistent with their having formed in a relatively shallow environment; the isotopic

composition of this argon would be inconsistent with recrystallization at depth if the deep brine present at the time of such recrystallization had been enriched in ^{40}Ar as are modern deep brines in the Palo Duro Basin. It is important to emphasize that the data rule out the possibility of any major recrystallization of the salt since the filling of the Palo Duro basin was essentially completed in the Triassic Period. If such recrystallization had occurred, it would be necessary that potassium and radiogenic argon had been distributed proportionately throughout most of the recrystallized material, a most unlikely possibility given the disparate natures of the two elements and given the presence of a lot of non-radiogenic argon that is distributed quite differently than the potassium.

4 CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

Silt-sized (>2 μm) silicate fractions separated from the lowermost Upper Permian, San Andres Formation, which is about 255 million years old, have illite crystallinity indices that indicate a high-temperature origin and potassium-argon apparent ages of about 345 million years (Ma). These data show that the material is detrital in origin and suggest that potassium-argon ages near 345 Ma are characteristic of the source material.

Mineralogical investigation of clay-sized (<2 μm) silicate fractions indicate that potassium is present in at least three minerals -- illite, K-feldspar, and chloritic material. Most of the potassium is in the illite. The sharpness of the illite peaks observed by x-ray diffraction would normally be interpreted as indicating illite formation at temperatures above 200°C, but since little is known about the character of illite that may form in an evaporitic environment, an authigenic origin for this illite cannot be ruled out. The apparent ages obtained for these fractions range from 254 Ma to 322 Ma, which suggests that they may be mixtures of authigenic illite and detrital material. The x-ray data, which show that these samples are composites of three types of potassium-bearing minerals, and a fairly evident inverse relation between the illite crystallinity index and apparent age for this set of samples are consistent with this concept of mixed ages. But the data available are not sufficient to show conclusively whether or not authigenic illite is present.

Typically, the clay-sized fraction of a shale has a potassium-argon age somewhat less than the (depositional) age of the rock, a consequence of the effects of diagenesis or burial metamorphism. That the apparent ages of the clay-sized material from the San Andres formation range upward from the depositional age implies a minimum of diagenetic change during burial and rules out the possibility of significant alteration of the illite long after deposition.

The salt specimens selected for potassium-argon analysis by stepwise dissolution have the characteristics of recrystallized bedded salt (Roedder, 1984). The potassium content of the dissolved salt was low (<100 mg/kg) and rather uniform from step to step except when the opening of millimeter-sized

fluid inclusions enhanced the amount of potassium. Large variations in ^{36}Ar content were observed; the largest amounts generally came neither from the outer portions of the specimens (in the first step of dissolution) nor from the larger fluid inclusions, but appeared to come from zones where mineral impurities were concentrated within halite crystals. These large amounts of ^{36}Ar indicate that some argon was trapped as gaseous argon, probably in a subsurface environment where gas pressure was greater than atmospheric pressure. But the amounts of ^{36}Ar in the millimeter-sized fluid inclusions are within the range to be expected for argon that had been dissolved in aqueous fluid in an environment having a partial pressure of ^{36}Ar similar to that of the atmosphere.

For each specimen analysed by stepwise dissolution there is a positive correlation between the ratios $^{40}Ar/^{36}Ar$ and $^{40}K/^{36}Ar$. Data points associated with the opening of millimeter-sized fluid inclusions show more deviation from the best-fitting lines than do most other points. Such deviation is thought to be an artifact of the experimental procedure, in which not all of the potassium from a fluid inclusion may be separated from the salt specimen in the step in which argon is released from the inclusion. The effect of this presumed carry-over of potassium from one step to the next may be eliminated by combining the data for the steps involved. If the data from certain steps are so combined, the correlation becomes very good for four of the five specimens analysed and the best-fitting lines for all specimens have similar parameters. For three specimens (SDS-6, -8, and -9), the isotope correlation lines may be interpreted as rather imprecisely determined isochrons having slopes corresponding to ages in the range 249 Ma to 281 Ma and initial $^{40}Ar/^{36}Ar$ ratios in the range 290 to 294. None of these lines differs significantly from a theoretical isochron for rock formed in mid-Permian time with atmospheric argon as the initial argon (assuming argon of the Permian atmosphere was not much different from modern atmospheric argon). The isotope correlation line for SDS-7 is well determined but appears to have been affected slightly by loss of some radiogenic argon from within or near the 3-mm long fluid inclusion that it contained. For SDS-5, the scatter of the data about the best-fitting line is greater than what is to be expected as a result of analytical error, so the line cannot be an isochron, but the conventional potassium-argon age for the whole specimen is 282 $\pm$ 43 Ma, indicating that the halite crystal is Permian in age.

If the hypothesis of carry-over of potassium from a large fluid inclusion into the next step is not correct, then it appears that some argon has migrated into these inclusions from the surrounding salt or that the inclusions have moved through the salt to a limited extent, picking up argon disproportionately to potassium in the process. But the good correlations obtained after combining data from selected steps and the consistency among the parameters for the isotope correlation lines so obtained show that potassium and argon have not moved over distances of more than a few millimeters within three of the five specimens since soon after the rock was formed. The two other specimens show some evidence of later disturbance, but the conventional potassium-argon ages, for the whole specimen in the case of SDS-5 and for individual steps in the case of SDS-7, show that such disturbance was probably minor.

Because of the very low potassium content of the salt specimens and because this work is the first in which stepwise dissolution of salt for potassium-argon analysis has been attempted, the data are not as accurate as in normal geochronometric work. But the data are sufficiently accurate to rule out major alteration of these salt specimens since the filling of the Palo Duro basin was (essentially) completed in the Triassic Period. The age values suggest that recrystallization of the salt in these specimens probably occurred rather soon after deposition. The correspondence of the intercepts of the isotope correlation lines with the $^{40}Ar/^{36}Ar$ ratio of atmospheric argon supports the idea of early recrystallization, since deep brines in the Palo Duro Basin may have obtained a significant radiogenic-argon component by water-rock interactions early in the history of the basin. These conclusions are consistent with the inference by Knauth and Beeunas (1986) that the isotopic composition of the water in most of the fluid inclusions in the Palo Duro salt is best explained as water incorporated during deposition or early diagenesis and that there is no evidence in the isotopic composition of the water that penetration of the salt by younger ground waters of meteoric origin has occurred.

Data obtained by crushing specimens that contained fluid inclusions show that such inclusions are enriched in potassium relative to the salt and that some of them contain radiogenic argon in amounts corresponding to apparent ages of hundreds of millions of years. The release of relatively large amounts of atmospheric argon in some cases made it impossible to detect radiogenic argon that may have been present in the inclusions, and the nature of

the crushing experiments precluded accurate measurement of potassium from those inclusions that had measureable radiogenic argon.

In summary, all of the data obtained in this study, from silicate materials and from salt specimens, including the fluid inclusions within the salt specimens, are consistent with a conclusion that the samples studied had not been recrystallized or otherwise appreciably altered since the filling of the Palo Duro Basin was completed in the Triassic Period. (The possibility of some later alteration of two of the salt specimens cannot be completely ruled out, but the probability of such appears to be quite low.) These data suggest that the post-depositional changes that have occurred within the rock have been low-temperature diagenetic changes, in which much of the salt was recrystallized fairly soon after deposition but in which there was little or no effect on the silicate minerals present in the rock. Except for one large fluid inclusion from which some radiogenic argon may have been lost later on, potassium and argon appear to have become fixed within the bulk of the recrystallized salt (at the two horizons from which salt specimens were taken for detailed study) within ten or so million years after deposition of the salt.

4.2 RECOMMENDATIONS

In order to determine whether authigenic illite is a significant constituent of the clays present in the San Andres Formation, a follow-up study should include a more detailed study of a smaller number of samples. ^{40}Ar-^{39}Ar studies of various size fractions (coarse enough that loss of ^{38}Ar by recoil would not be important) could provide information about the apparent ages of the feldspars and the coarser illite (Sedivy *et al.*, 1984). Conventional potassium-argon ages for clay samples separated into narrow size ranges below 2 μm, which may conveniently be obtained by the microanalytical technique (Wampler *et al.*, 1985), should show whether there is a major, fine-grained illite component about 255 million years old, which would be evidence of the presence of authigenic illite, or whether there is a continuous range of apparent ages for the finer illite, which would suggest that such illite is detrital material slightly altered by diagenesis. Since an appreciable amount of potassium is present in much of the chloritic material, potassium-argon analyses of isolated chloritic material could indicate whether such material formed by alteration of detrital illite or whether authigenic illite layers

formed contemporaneously with the chlorite. Such a study should be complemented by scanning electron microscopy with energy-dispersive x-ray analysis of the materials.

The results obtained by stepwise dissolution of salt show that this new method has great potential for geochronometric study of rock salt of low potassium content. The experience gained in the first set of analyses by this method provides a basis for improved accuracy in future work. The anomalous concentration of argon in recondensed water within the dissolution apparatus, which was a significant problem in the present study, can be avoided by a change in design of the apparatus. The problem of carry-over of potassium from one step to the next can be minimized by not terminating steps immediately after large fluid inclusions open, but rather continuing each such step until it is reasonably certain that all potassium from the opened inclusion has been washed from the specimen. Improved precision in the parameters of the isotope correlation lines may be obtained by using somewhat larger specimens to ensure that enough ^{36}Ar for accurate measurement is released in each step. With larger amounts of ^{36}Ar available for measurement and with frequent calibration runs, the accuracy of measurement of $^{40}Ar/^{36}Ar$ could be improved so that the relative error for measured values of this ratio is a few tenths of one percent. (Probably, better accuracy and better sensitivity could be achieved with new equipment.) Such an improvement would permit accurate determination of slopes for isotope correlation lines even in cases where the range of observed $^{40}Ar/^{36}Ar$ values is small. It would also allow the intercepts of the correlation lines to be determined with high accuracy.

As implied near the end of the discussion of the potassium-argon data (Section 3.4), it is not clear that any of the salt specimens specimens analysed in this work would have met the criteria necessary for interpretation of their isotope correlation lines as isochrons, had the correlation lines been precisely determined. But if the variability in the parameters of the isotope correlation lines has been largely a matter of analytical error, rather than a failure of the specimens to have met the assumptions of the isochron method of dating, then the improvements in method suggested above might allow the age of the Palo Duro salt to be determined with an uncertainty of only a few million years. Furthermore, it might be possible to establish a slight difference between the initial argon in the salt and modern atmospheric argon. (Although the difference in $^{40}Ar/^{36}Ar$ between the Permian atmosphere and the modern

atmosphere may not be detectable when the error of measurement is about one percent, the difference should be detectable if the error is reduced to a small fraction of one percent.) Since it appears that some portions of the salt are particularly rich in argon, to the extent that their radiogenic argon content is negligible, it would be very useful in interpretation of the age of the salt in which such concentrations of argon occur to be able to distinguish between Permian atmospheric argon and modern atmospheric argon.

It would not be surprising to find that more accurate analyses do not substantially improve the way potassium-argon data from recrystallized salt fit isotope correlation lines, because it seems rather unlikely that such salt should have become closed to potassium and argon at a well defined time with isotopically uniform argon throughout. But more accurate data would allow more confident interpretation of the way in which the salt specimens may have departed from the conditions required for dating by the isochron method, and thus should provide some information about the environment in which the salt recrystallized or about later disturbances that may have affected the salt. Although the data of the present study rule out any major, recent recrystallization of the salt at the two levels of the Grabbe #1 well from which salt specimens were taken, the possibilities of minor, recent disturbance at these levels and of recent disturbance of salt at other levels cannot confidently be ruled out without more accurate and more extensive analytical work.

Accurate measurement of the concentration of ^{36}Ar in fluid inclusions should be very useful in interpreting the origin of the included brine (Zaikowski et al., 1987), so it would be useful to have more work on specimens having fluid inclusions large enough that their volumes and argon contents can be accurately measured. In addition to potassium-argon measurements, neon, helium, and uranium should be measured. When an inclusion is millimeter-sized or larger, it appears that data obtained by carefully controlled stepwise dissolution might show reasonably well how much of these elements are present in the inclusion, but the contents of the inclusion could never be completely distinguished from that of the surrounding salt by this method. If a better apparatus were constructed to allow large inclusions to be opened physically, in vacuum, in a controlled way, very useful information about the distribution of the inert gases and their radioactive progenitors should be revealed. It may be possible to physically separate the salt formed by evaporation of water from a large inclusion (dimensions of at least a few millimeters) from the

halite that originally surrounded the inclusion, so that the potassium and uranium contents of that salt can be measured. Even better would be a device that could withdraw the brine from an inclusion before the water has a chance to evaporate appreciably. Since there are components available commercially that would allow for viewing and manipulation of a specimen within an ultra-high vacuum chamber, it should not be particularly difficult to construct an apparatus for controlled withdrawal, in vacuum, of fluids from relatively large inclusions.

A final recommendation is that the stepwise dissolution procedure for potassium-argon analysis should be applied to specimens of primary bedded salt, if sufficiently large specimens of such salt can be obtained. If the sensitivity and accuracy of the analytical methods can be improved enough to obtain accurate data from such specimens, then it may be possible to accurately date sedimentary salt formations and to determine the isotopic composition of argon in the atmosphere under which the salt precipitated.

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APPENDIX

DETAILED DESCRIPTION AND DISCUSSION OF POTASSIUM-ARGON ANALYTICAL PROCEDURES

Introduction

As originally envisioned, the apparatus for stepwise dissolution would have been designed so that the salt to be dissolved would have remained in one place, and the brine formed by dissolution of the salt would have drained into a moveable container. After each step in the dissolution, an empty container would have been moved into place to collect the brine formed during the next step. Later it was realized that a simpler apparatus could be used, if the specimen were moveable rather than containers for brine. In the simpler apparatus (Figure 3-1), the brine drains into one of five fixed chambers, called sumps, during each step of the dissolution, and the specimen is moved from sump to sump between steps.

Although earlier work in this laboratory provided a good bit of information about the behavior of argon released by dissolution of salt under vacuum, the new procedures used in this study were under development as the work progressed. Not all aspects of the procedures were well defined at the outset of the work, so changes in procedure were introduced as the need for them became evident. Consequently, the description of procedures that follows necessarily includes some discussion of phenomena observed during the analyses that led to changes in procedure. Also included are some interpretations made after the laboratory work had been completed, which provide a basis for significant changes in procedure in any future work.

Loading and Evacuation of the Apparatus for Stepwise Dissolution

To prepare for a stepwise dissolution experiment, 1 ml of distilled water is put into each of Sumps 1, 2, and 3. (In the first experiment, 10 ml of water was used, all in Sump 1, but it soon became evident that degassing of the water is easier if a minimal amount of water is used and it is distributed among several sumps). A salt specimen is then placed in Sump 5 and the apparatus is sealed.

Before evacuation, the finger of the cold trap is filled with dry ice, preferably with some ethanol to maintain good heat exchange between the glass and the evaporating dry ice. After other valves are set to direct flow to a mechanical vacuum pump, the valve C1 is opened. Soon, as pressure in the apparatus drops, the gases dissolved in the water cause effervescence. The rate of effervescence decreases quickly, and, without mechanical stirring, degassing of the water would become very slow. Stirring the water in each sump (1, 2, and 3) by moving the pedestal up and down rapidly for a brief period (about 30 seconds) allows most of the gas remaining in the water to escape; then valves are used to bring a diffusion pump in series with the mechanical pump. Further stirring of the water in each sump for brief periods over a total of several minutes reduces the amount of gases remaining in the water sufficiently that further release of argon may be monitored with the mass spectrometer.

At all times after evacuation of the apparatus has begun, except when it is intended for the salt to be dissolving, it is important to keep the salt specimen warmer than the water in the apparatus. Otherwise, water would condense on the salt and slowly dissolve it. During evacuation, the water in the apparatus is cooled by evaporation as water vapor moves to the cold trap. But after valve C1 has been closed, the coolant is removed from the cold trap to allow the accumulated ice to melt. A convenient way to keep all the water cold after the cold trap has warmed up is to cool one of the sumps with ice water. This keeps the water-vapor pressure in the apparatus at a value well below that where water would condense on the salt (which remains at room temperature). Under the reduced vapor pressure, evaporation keeps any water that is not in the sump surrounded by ice water well below room temperature. In time, all such water will evaporate and recondense in the cold sump.

Elimination of Contaminating Argon

A major goal of this work has been to determine whether the $^{40}Ar/^{36}Ar$ ratios of argon released by stepwise dissolution of each salt specimen are correlated with the corresponding $^{40}K/^{36}Ar$ ratios in a way that would define a potassium-argon isochron for the specimen. In such work it is essential that argon from sources other than the specimen should not affect the data for the specimen significantly (Hayatsu and Carmichael, 1977). It is also important

that argon from the atmosphere that may superficially contaminate the specimen as a consequence of its handling and preparation be eliminated before dissolution begins.

In the absence of prior information about the amount of argon in the salt, a satisfactory criterion for the amount of contaminating argon that may be permitted (from sources other than the specimen) can be based on the detection limit for ^{36}Ar. In this work, the minimum uncertainty in measurement of ^{36}Ar was equivalent to about 0.1 fmol (1 fmol = 10^{-15} mol), so contaminating argon (in which ^{40}Ar is about 300 times more abundant than ^{36}Ar) is negligible if it amounts to less than 30 fmol.

There are several potential sources of contaminating argon (other than the specimen itself) within the dissolution apparatus: 1) leaks, 2) degassing of the apparatus, and 3) degassing of the water. Leaks sometimes develop in an apparatus of this sort, usually where dissimilar materials are joined, but such leaks are normally quite evident in tests carried out before an analysis begins. No evidence of leaks in the dissolution apparatus was observed during the course of this work.

Tests of the apparatus carried out with neither water nor salt present have shown that degassing of the material of the apparatus (which would include any virtual leaks) should not normally be a significant source of argon, a result that is supported by a lot of prior experience with similarly constructed apparatus. But there are two important caveats associated with this conclusion. First, heating the apparatus will cause degassing of argon, and the amount of argon so released may be significant unless the apparatus was earlier heated under vacuum to a higher temperature. Second, mechanical strain may release argon from within materials. The dissolution apparatus was heated (with an air gun) under vacuum after it was constructed, and blank runs have demonstrated that further heating has not been necessary, even though some exposure of the inner walls to air occurs whenever a new specimen is loaded. Very rarely, in other parts of the apparatus for argon isotopic analysis, the stress occasioned by closing or opening a valve has produced a pulse of gas, including argon, which presumably escaped from an interstitial location between metal crystals. Such occurrences are unpredictable, but they are so infrequent that a spurious result from this cause is unlikely. Finally, it is possible that abrasion of glass might release some argon when a pedestal is manipulated with magnets, but there has been no evidence in this work of appreciable abrasion.

As noted in the section above, degassing of water is a very slow process after there is no longer enough dissolved gas to cause effervescence. Diffusion of argon through water is so slow that some active mechanism must be used to get dissolved argon out of the water in a reasonable period of time. Vigorous stirring is effective, but it is not an elegant way to release such argon, and it may cause some abrasion of the glass. Distillation of the water provides a simple way to release dissolved argon, and it was expected that only a very small fraction of the released argon would re-dissolve in the distillate. Distillation is easily effected by cooling an initially dry sump with ice-water. Over a period of several hours, water will evaporate from other parts of the apparatus and condense in the sump cooled by ice-water. If water at or a little above room temperature is used to supply heat to the sump(s) from which water is evaporating, the distillation can be completed in a shorter time. Calculations based on the Henry's Law coefficient for argon show that, volume for volume, argon in equilibrium between water and gas should be much more abundant in the gas phase (by a factor of 17 at 0°C). Since the volume of the dissolution apparatus is many (50-100) times the volume of water used in this work, it was expected that each distillation should reduce the amount of residual argon by a factor of the order of 1000. In fact, the distillation procedure was not nearly so effective, for reasons that were not understood until the work had been completed. Nevertheless, repeated distillation could be used to reduce the amount of residual argon to a negligible level. In practice, distillation was typically stopped when the amount of argon released by distillation was less than 300 fmol. It was assumed that the amount of argon remaining in the water would then be less than 30 fmol.

No experiments have been done with a salt specimen in the apparatus without water, which could show how argon degasses from the salt under vacuum. But experience has shown that by the time the argon in the water has been reduced to a negligible amount, degassing of the salt is no longer important as a source of argon. This is in contrast to the behavior of ordinary rock specimens, which generally will evolve argon for days after being placed under vacuum unless they are heated to speed the process. The difference is presumably a consequence of the impermeability of rock salt, in contrast to the character of most rocks in which low solubility and a high degree of brittleness can contribute to the formation of an intricate network of very fine pores within the rock. It is standard practice in conventional potassium-

argon work to "bake" rock samples under vacuum before analysis, but such heating was avoided in this work for several reasons. Most important of these reasons is the likelihood that heating might have altered the distribution of argon within the salt specimens. Since blank runs have shown that the rate of degassing of argon from the salt is negligible by the time the water is thoroughly degassed, the only reason one might consider for baking the specimens would be speculation that atmospheric argon might have become trapped in the salt during handling and preparation in such a way that gentle heating would release it without appreciably disturbing the distribution of other argon in the salt. It seems reasonable to expect that any contaminating argon that may have been trapped in this way should be near enough to the surface that it would be released during the first dissolution step. So instead of heating the specimens on the chance that contamination could be so eliminated, the approach used in this work has been to consider the data from the first dissolution step to be suspect in regard to the possible occurrence of contaminating argon.

Stepwise Dissolution and Transfer of Argon for Analysis

After the contaminating argon in the apparatus has been reduced to a negligible level, as shown by "blank" analyses, the first step in dissolution of the sample can begin. As noted above, a salt specimen will gradually dissolve by deliquescence if the liquid water in the apparatus is at the same temperature as the salt, but such dissolution proceeds very slowly. In order to hasten the dissolution, the sump containing the specimen may be cooled so that water condenses on the glass around the specimen. If the specimen is touching the glass, some of the condensing water will flow onto the salt. An effective way to control the condensation of water is to hold a small piece of dry ice against the outside of the glass so that water accumulates inside the glass near the point of contact. As in the distillation of water to remove contaminating argon, described above, the condensation of water proceeds more rapidly if the sump containing the evaporating water is surrounded by water, at or a little above room temperature, to act as a heat source.

The dissolution procedure begins with the salt specimen atop the pedestal in Sump 5. Since the area where water condenses may be controlled with the dry ice, and since the specimen may be moved to a limited extent, it is possi-

ble to control to a certain degree which part of the specimen dissolves most rapidly. As more water condenses, the brine formed by dissolution of salt drains downward into the sump. To terminate the dissolution, it is necessary only to stop cooling the glass near the specimen and to cool one of the other sumps (not the one to which the specimen will next be moved) with ice water. The reduction of water-vapor pressure caused by the cool sump promptly stops condensation of water on the specimen, and the liquid remaining on the specimen quickly evaporates. Using magnets to control the pedestal, the specimen is then lifted out of its sump and either transferred to the next sump or left poised between the two sumps. After the argon released in the first step has been analysed, and any following blank runs have been completed, the following dissolution steps are carried out in the same manner as the first. The only exception is that in the last step the specimen may be placed in the bottom of the sump rather than on a pedestal. In such a case, some stirring is usually required to effect complete dissolution.

As noted in Section 3.2.1, the brine cannot drain completely from a specimen as a dissolution step is brought to a close. The film of water that does not drain from the specimen will evaporate, leaving a small amount of once-dissolved salt to be carried over with the specimen to the next sump. Thus, the potassium released in one step is not completely separated from that released in the subsequent step. If potassium were uniformly distributed in a specimen and if the amount of salt dissolved per step were kept reasonably constant, this problem should have only a minor effect on the results. But in this study, the amount of salt dissolved per step was often quite variable, and the data show that potassium was in some cases distributed non-uniformly, so the carry-over of potassium from one step to the next may have had an important effect on the results.

It was expected that there would be little trouble effecting a complete separation of the argon released in one step from that to be released in the subsequent step (but this expectation turned out to be incorrect). The apparatus was designed so that argon in the gas phase should be swept almost completely out of the apparatus when the valve C1 is opened to transfer the argon to the manifold where it is mixed with the reference isotope ^{38}Ar and purified prior to isotopic analysis. Whenever C1 is to be opened for transfer of argon, the cold trap within the apparatus is first cooled with dry ice. Argon is then swept toward the cold trap as a consequence of the flow of water vapor

to the cold trap, the water vapor acting in the same way as the vapor in a diffusion pump. Earlier work in this laboratory had shown that flow of water vapor through a capillary is fully effective to sweep argon out of the portion of the apparatus that is upstream from the capillary. There is no indication in the data obtained in this study that the sweeping action did not act as expected for argon that was in the gas phase, but there is plenty of evidence that a significant portion of the argon released by a dissolving sample may remain dissolved in the liquid and not be affected by the sweeping action.

In the first dissolution step for the first specimen, a special circumstance (the specimen got stuck beside the pedestal during the attempt to move it to the next sump) made it impossible to stir the brine that had drained to the bottom of the sump during dissolution. The argon in the gas phase was transferred from the apparatus for analysis, and then the valve C1 was closed. The water from the brine that had formed was distilled to another sump overnight, and a "blank" argon analysis was performed the next day to see if a significant amount of argon had been dissolved in the brine. It was a surprise to find almost as much argon in the blank run as in the original analysis. In both analyses, the argon was enriched in ^{40}Ar relative to atmospheric argon, and the amount of radiogenic argon in the blank run was nearly as great as in the original analysis, so it is clear that most of the argon in the blank run was argon released from the specimen during the first dissolution step but not released from the brine. (No further dissolution of the specimen had occurred overnight, because the sump to which the water from the brine was distilled had been kept cold throughout the period.) In retrospect, this phenomenon is not hard to understand, because observation of pressure changes during gas transfer have indicated that the amount of gases other than argon released by dissolution of these salt specimens is generally quite small. Usually there was no bubbling action in the brine as it formed, and it is evident that molecular diffusion is not very effective in getting argon out of the brine in a short time. A second blank run, after the water in the apparatus was again distilled from one sump to another, showed that a small fraction of the argon from the sample had been retained in the apparatus during the second transfer of argon (for the first blank run).

In the later dissolution steps for the first specimen, the brine formed was stirred by moving the pedestal up and down vigorously before transfer of the argon for analysis. Blank runs following the analyses showed that stir-

ring is effective in getting most of the argon out of the brine. For all the other specimens, the distillation procedure described in the section above was routinely used as a means of releasing argon from the brine formed in each step. A blank run was usually carried out after each step in the dissolution of a specimen. These blank runs indicated that the distillation procedure was not as effective as it had been expected to be, but the reason for this was not understood until after the analytical work had been completed.

As indicated above, a complete distillation of water containing dissolved argon, in this apparatus, should leave only about one-tenth percent of the argon dissolved in the recondensed water. But the blank runs carried out in this work show that the amount of water retained in the recondensed water was typically from one to ten percent of the argon that had been in the apparatus during the distillation. The key to understanding this phenomenon came from a review of all the data, which showed a correlation between the rate of distillation and the relative amount of argon dissolved in the recondensed water. In those cases where the distillation was allowed to proceed slowly during the night, with no heat source other than air for the sump from which the water was evaporating, the amount of argon retained in the water (as seen in the blank run following the original transfer of argon out of the apparatus) was three percent or less of the original amount of argon. When the distillation was done more rapidly, by providing a source of heat to the sump from which the water was evaporating, the amount of argon in the succeeding blank run was from three to ten percent of the original amount of argon. Since the percentage of argon dissolved in the recondensed water was in all cases greater than the expected equilibrium amount, and since that percentage is directly related to the rate of distillation, a reasonable explanation of the phenomenon is that the flow of water vapor during distillation concentrates argon in the space immediately above the condensing water, so that more argon is dissolved in the water than would be dissolved under equilibrium conditions. The mechanism for concentrating the argon is presumably the same as that which causes argon to be swept out of the dissolution chamber when water vapor flows to the cold trap -- the same as the action of flowing vapor in a diffusion pump. Although the vapor does not flow through a capillary during the distillation, the rate of flow must be sufficient to create a dynamic steady state in which argon is considerably enriched in the sump where water is condensing. If this interpretation is correct, a simple solution to the problem is to use a cold

finger above each sump for the condensation of water so that the water vapor does not flow into a "dead end" where argon may be appreciably concentrated.

There is another possible explanation of the relatively large amounts of argon found in the blank runs. This possibility is that argon was trapped in the ice that formed in the cold trap as gases were transferred out of the dissolution apparatus, rather than having been concentrated in the recondensed water. Trapping of argon by ice that forms in a cold trap at liquid-nitrogen temperature (-196°C) is a well-known phenomenon, but Wampler and Yanase (1974) reported that argon is not so trapped by ice forming in a cold trap cooled by a melting-ethanol slush (-112°C). Ice forming in a trap cooled by dry ice (-79°C) should be even less prone to trap argon than when an ethanol slush is used. But since the amount of ice and the rate at which it formed were greater in this work than in the earlier experiments that showed trapping of argon by ice to be negligible (at -112°C), the possibility that the ice trapped some of the argon in this work must be considered. Such trapping would be most likely during the brief period between the time when the trap is first cooled with dry ice and when the valve C1 is opened for transfer of the gases. During this period, argon will become concentrated in the portion of the apparatus comprising the cold trap and the tube leading to the valve, because of the action of the flowing vapor. But that volume is much greater than the volume of ice formed, so it does not seem likely that a significant amount of argon would end up within the ice. No experiments were done during the course of the analytical work to show conclusively whether or not an appreciable fraction of the argon in the apparatus can be trapped in the ice, but a later experiment showed that such trapping is not important. In this experiment a portion of the isotopic reference material (^{38}Ar) was introduced into the dissolution apparatus (by trapping it in ice formed with the cold trap at liquid-nitrogen temperature, then allowing the trap to warm up), which contained about one milliliter of water. With the valve C1 closed, the trap was cooled with dry ice and kept cool until all the water had distilled to form ice in the trap. The ^{38}Ar was then transferred out of the apparatus. A subsequent blank run showed that none of the ^{38}Ar had been trapped in the ice formed at dry-ice temperature.

Isotopic Analysis of Argon

The transfer of argon from the dissolution apparatus, to be mixed with the reference isotope and purified, and the transfer of the purified mixture to the mass spectrometer, have been described in Section 3.2.2. After the transfer of argon to the mass spectrometer is complete, a valve leading to the diffusion pump is opened so that the manifold where the argon had been purified may be evacuated in preparation for the next analysis. The valve C1, which connects the dissolution apparatus to the manifold, is left open at the beginning of this evacuation to ensure that any argon in the dissolution apparatus (in the gas phase) is pumped away. After three minutes C1 is closed and the next step in the dissolution procedure may begin. (In the analyses of the first specimen studied in this work, C1 was closed before transfer of argon to the mass spectrometer, because it was assumed that the flow of water vapor would carry all gaseous argon out of the dissolution apparatus. But a blank run showed that nearly one percent of the ^{38}Ar reference material that had been mixed with a sample of gas was sealed in the dissolution apparatus by closing C1 at this stage. Apparently the flow of water vapor beyond the cold trap in the dissolution apparatus is not sufficient to sweep argon effectively out of the small portion of the apparatus that is between the trap and the valve. The procedure was then changed so that this portion of the apparatus would be evacuated along with the manifold to which it connects.)

The isotopic analysis is carried out by scanning over the argon mass spectrum according to a procedure that is standard in this laboratory. The procedure allows graphical averaging to be used to compensate for a very small instrumental drift and provides two independent sets of data for the argon isotope ratios so that any mistakes in reading the data are likely to be recognized. The sensitivity of the instrument is usually not quite the same for the different isotopes of argon (mass discrimination), so the raw data are corrected on the basis of calibration runs in which atmospheric argon is used as a reference material to determine the relative sensitivity of the instrument for ^{36}Ar and ^{40}Ar. The ratio $^{40}Ar/^{36}Ar$ in atmospheric argon is assumed to be 295.5 (Steiger and Jäger, 1977). The sensitivity for argon is assumed to vary linearly with mass, so that the sensitivity for ^{38}Ar equals the average of the sensitivities for the other two isotopes. Experiments done after the stepwise dissolution work had been completed, in which known amounts of

the reference isotope have been mixed with small, essentially constant amounts of air, have shown that the degree of mass discrimination varies with the pressure of argon (which is the major gas present under normal conditions) in the mass spectrometer. It has been possible to model rather accurately the mass discrimination observed in the calibration runs by assuming that the effect of the pressure of argon (proportional to the amount of argon in the mass spectrometer) on mass discrimination has been temporally constant since the mass spectrometer's ion source was modified after the first salt specimen in this work had been analysed, that there is a pressure-independent mass discrimination effect that does change (slowly) with time, and that there is a small degree of non-linearity in the response of the ion-current detector (a so-called voltage coefficient).

The mass spectrometer has a small, but persistent, background spectrum in the argon mass range that is caused by organic molecules. Usually, this background has only a small effect on the measurement of ^{36}Ar and no significant effect on measurement of the other argon isotopes. Since the major peaks in the mass spectrum of the organic material are at odd mass numbers, a correction for the effect of the background spectrum may be made from measurements of the signals at these odd mass numbers. Normally the magnitude of this correction is so small that uncertainty in the accuracy of the correction is of no consequence. Occasionally, and particularly after the filament in the ion source has been replaced, HCl will contribute to the background spectrum. The effect of HCl decreases steadily with time, so correction for its presence can be made from background scans of the argon mass range made when no argon is present. Normally the effect of HCl on the background spectrum is negligible.

The results of the calibration runs with atmospheric argon, after corrections for mass discrimination according to the model described above, indicate that the relative error in measurement of the ratio $^{40}Ar/^{38}Ar$ should not be more than about one-half percent under normal conditions. When there is sufficient ^{36}Ar present, the error in the measured ratio $^{36}Ar/^{38}Ar$ should not be more than one percent. But when the amount of ^{36}Ar is very small, the noise inherent in the weak signal and any uncertainty in the magnitude of the correction for the background spectrum appreciably enhance the relative error of measurement. The error estimates that appear in the tables of data in Section 3.3.3 are based on a one-half percent error in the ratio $^{40}Ar/^{38}Ar$ and a one

percent or greater error in the ratio $^{36}Ar/^{38}Ar$, the latter depending on the precision possible in reading the ^{36}Ar signal and correcting it for the effect of the background spectrum.

After the analyses of the first salt specimen had been completed, but before the analyses of the second specimen had started, the filament of the mass spectrometer failed. It is characteristic of the mass spectrometer to have a somewhat degraded performance for some time before the failure of a filament (when that failure is a consequence of normal evaporation of metal from the hottest part of the filament, rather than a consequence of an accident). The most obvious manifestation of the degraded performance is an increasing "sharpness" of the tops of the peaks in the mass spectrum, which is associated with an apparent decrease in stability and a variability in the relative sensitivities for the different isotopes of argon (that is, changes in the magnitude of mass discrimination). The mass spectrometer record for the first specimen shows clear evidence of such degradation in performance, and data obtained in calibration with atmospheric argon show that the degree of mass discrimination changed by an unusually large amount prior to the failure of the filament. For this reason the estimated errors in the argon analyses for this specimen are greater than for the other specimens.

At the time a new filament was installed, a small modification in the configuration of the mass spectrometer's ion source was made in an attempt to reduce the degree to which the ion source traps argon, causing a slight carryover of argon from one analysis to the next -- a so-called memory effect. This modification (which was actually a return to the originally designed configuration of the hole that limits the size of the electron beam passing through the ion source) was successful in reducing the magnitude of the memory effect, but it caused a reduction in sensitivity as well. The sensitivity could be restored to a satisfactory level by changing the potential of the ion repeller (relative to the chamber where ions are formed, called the cage) from the 1 V setting that had been used to a value near -1 V. An examination of the data provided by the manufacturer of the MS-10 mass spectrometer indicates that problems caused by mass discrimination are more likely when the ion repeller is negative with respect to the cage, but a consideration of the physical relationships involved suggested that these problems are a consequence of a variation in the ratio of ion-repeller voltage to cage voltage that occurs as the mass spectrometer scans across the mass spectrum. By

changing the voltage divider network so that this ratio of voltages remains constant, problems with mass discrimination should be minimized. Such a change was made, and the calibration data obtained since the change indicate that mass discrimination changes only slowly with time and can be modelled accurately as described above.

Whenever the mass spectrometer has been opened for a change of filament, enhancement of the background spectrum caused by organic material is observed. The background spectrum decreases in magnitude slowly, returning to normal levels after several weeks. For this reason, the corrections applied to remove the effect of the background spectrum were greater than normal for the first few specimens analysed after the filament change. In the case of SDS-6, the first such specimen, the uncertainty of the ^{36}Ar measurements was appreciably increased because of the larger-than-normal correction for the background.

Potassium Analysis

When the stepwise dissolution of a specimen has been completed, the salt accumulated in each sump is removed and prepared for potassium analysis as follows. A torch is used to open the glass tube above each sump; through this tube distilled water is added as needed to dissolve the salt in the sump and the resulting brine is removed by pipette. More distilled water is used to rinse the sump, at least twice, and the brine and wash water (totalling 25-30 ml) are combined and centrifuged to separate any insoluble residue from the liquid. The liquid is then poured off into a pre-weighed fluorocarbon beaker, from which the water is evaporated, to leave dry salt. (Only traces of insoluble residue were left by these specimens, so it was not necessary to rinse and re-centrifuge the residue to get a satisfactory "yield" of salt.)

Each sample of dry salt is weighed in the fluorocarbon beaker from which the water was evaporated. Then the salt is dissolved in water containing a small amount (2.5 mmol/kg) of CsCl and transferred to a pre-weighed polyethylene bottle. More of the CsCl solution is used to rinse the beaker, and the rinses are added to the solution in the bottle. Finally, more of the CsCl solution is used to bring the mass of solution in the bottle to one hundred times the mass of the original salt. (In a few cases where the mass of salt was less than 0.1 g, a relatively larger amount of solution was used. One

sample solution had to be further diluted because its potassium concentration was greater than the maximum potassium concentration, 2.0 mg/kg, in the set of reference solutions.)

The potassium content of each solution was determined by atomic absorption spectrophotometry, by comparison with reference solutions having nominal potassium contents of 0, 0.5, 1.0, 1.5, and 2.0 mg/kg. These solutions were prepared by dilution of a primary reference solution (prepared from reagent-grade KCl) with water. CsCl and NaCl were added in amounts appropriate to match the sample solutions. For this purpose it was assumed that the salt samples are virtually pure NaCl, and the reference solutions were made to contain 10 g/kg of NaCl. Unfortunately, at this level the potassium content of the salt added to the reference solutions is not negligible. The ACS reagent-grade NaCl available for this work contains about 10 mg/kg potassium, which would have contributed an extra 0.1 mg/kg potassium to each reference solution. To minimize the contribution of potassium from the NaCl, the reagent-grade NaCl was partially recrystallized from distilled water, twice, to reduce its potassium content. The reference solutions were then prepared from the twice-recrystallized salt. Because the amount of potassium contributed to the reference solutions by the recrystallized salt was unknown, the absorbance data from the set of reference solutions was analysed in the manner of the method of standard additions, using readings obtained during aspiration of distilled water to establish the instrumental zero. The results indicate that the salt contributed 0.04 mg/kg potassium to each reference solution (corresponding to 4 mg/kg potassium in the recrystallized salt). The potassium content of each reference solution was accordingly corrected before the working curve was established for determination of the potassium contents of the sample solutions.

The uncertainty in the potassium content of each reference solution is about 0.01 mg/kg, and there is an uncertainty of similar magnitude in the instrumental readings. Blank runs indicate that contamination typically contributes roughly 0.01 mg/kg potassium to a sample solution. The overall error in the potassium measurements is estimated to be 0.02 mg/kg in the sample solutions, which corresponds to a relative error in the potassium content of the salt samples that ranges up to 5 percent for those samples having the lowest potassium content, about 40 mg/kg (0.004%).

There is an additional source of error that affects the potassium contents when they are expressed as mass fractions. The dry salt samples were weighed only to the nearest 0.01 g, so the relative error in the amount of salt can be quite large. Typically, in the first step of dissolution of a specimen the amount of salt dissolved was 0.10 g or less. In such cases the relative weighing error is unusually large. This source of error does not affect the potassium-argon ratios, since any weighing error affects the specific argon content equally as it affects the potassium content.